OUTLINES OF GENERAL CHEMISTRY

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OUTLINES

OF

GENERAL CHEMISTRY

BY

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AUTHOR'S PREFACE

THE present edition of the "General Outlines" differs in many important respects from its predecessors. The reproach has always been levelled against the "Outlines" that it, in contrast with my other books, is too "difficult"; and, although so recently as in the last edition I expressed my inability to remedy this defect, I have since then borne in mind this just reproach. Accordingly, in the present edition, I have directed my energies in the first instance towards bringing this book more into line with the others. If I may accept the verdict pronounced upon portions of the book while passing through the press, these disadvantages to the reader have been successfully overcome.

The mechanical aids, as the division into short sections provided with headlines, and the use of spaced type to emphasise important ideas in the text, will meet the eye of even the casual reader. In additon, the whole text has been carefully revised with the same object in view, and I hope that I have succeeded in rendering the book more readily accessible.

Not only have I made important changes in the arrangement of the whole, and in the development of the fundamental principles of chemistry in accordance with the evolution of the science, but I have also introduced several new chapters, on ions in gases and radioactivity, and on colloids. The justification of the title selected for the latter chapter, microchemistry, will be found there. It will then be observed how naturally this subject, the phenomena of which are primarily conditioned by surface-energy, takes its place alongside of the older subjects of thermochemistry, electrochemistry, and photochemistry.

The elaboration of the material of these new subjects for the purpose of presenting a summary of their fundamental principles in the "General Outlines" has not been without marked influence on my own scientific development. I am now convinced that we have recently become possessed of experimental evidence of the discrete or grained nature of matter, which the atomic hypothesis sought in vain for hundreds and thousands of years. The isolation and counting of gas ions, on the one hand, which have crowned with success the long and brilliant researches of J. J. Thomson, and, on the other, the agreement of the Brownian movements with the requirements of the kinetic hypothesis, established by many investigators and most conclusively by J. Perrin, justify the most cautious scientist in now speaking of the experimental proof of the atomic nature of matter. The atomic hypothesis is thus raised to the position of a scientifically well-founded theory, and can claim its place in a text-book intended as an introduction to the present state of our knowledge of General Chemistry.

That I have considered it expedient to give it this place in the above-mentioned new chapters, in which the proofs are to be found, is scientifically justifiable. From the point of view of stoichiometry the atomic theory is merely a convenient mode of representation, for the facts, as is well known, can be equally well, and perhaps better, represented without the aid of the atomic conception as usually advanced. In this part of the book, then, I have made little use of the atomic theory; but it is only natural that it should be developed at a stage where the experimental evidence is considered. I trust, therefore, that the expert will find something new in this direction at the place indicated.

In conclusion, I must confess that I could not have undertaken the heavy task, which the preparation of this edition has entailed, had I not been assured of the untiring and sympathetic assistance of Dr. Karl Drucker. To him I am indebted not only for a recalculation of atomic weights, but also for countless suggestions and reminders, which often led to extensive rearrangement of the text. In particular, he was ever on the watch lest the goal, the conversion of the old "Outlines" into a readable book, should be lost sight of.

WILHELM OSTWALD.

GROSSBOTHEN,
November 1908.

TRANSLATOR'S PREFACE

The present English edition is a translation of the fourth German edition, which, as Professor Ostwald has said, has been thoroughly revised and largely rewritten. The additions and alterations alluded to in the preface refer only to the previous German edition. Even a cursory comparison of the present English version with its predecessor will indicate the very extensive additions which have been made. Not only have new chapters on gas ions and radioactivity, and on colloid chemistry, been added, but Book III. on Chemical Kinetics and Equilibrium, and Book IV. on Electrochemistry are practically new, occupying close on one hundred pages each, as against thirty and twenty-five pages in the previous edition.

The revised proofs of the translation have passed through Professor Ostwald's hands—a guarantee of its substantial accuracy. The translator is indebted to Professor James Walker for permission to use the earlier translation wherever applicable, and desires also to express his thanks to his colleague, Mr. I. Hoppenstein, B.Sc., for suggestions and kind assistance in reading the proofs.

1912.

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MATTER

CHAPTER I

THE LAWS OF CONSERVATION

CHEMISTRY is that branch of Natural Science which deals with the specific properties of objects. We designate as objects those parts of the external world which are differentiated by their properties from their surroundings in such a manner that the sum of these properties can be moved from place to place. Such properties as remain together unchanged, as colour, shape, weight, we call specific properties. By properties are understood all the relations into which the object can be brought to our organs of sense, as well as to other objects. Colour is a relation of the object to the human eye, weight is a relation in which it stands to the earth's sphere. While relations of the first kind are direct, the latter, to be perceived, must be converted into relations of the first kind. We cannot directly perceive the weight of a body, nor can we recognise it by any other sense; but we do so if we see it fall, or if we try to lift it from the ground, and feel the muscular exertion.

The investigation of properties takes place in two directions. We may keep the object under unchangeable or constant conditions, and estimate accurately the properties which it possesses under these conditions. The results of this method form the immediate foundation of our knowledge of objects. Or we may alter the conditions under which the object exists in a definite and known manner, and ascertain whether and to what extent the properties also change. This is a larger and more complicated problem than the other, but it is at the same time much more important. The former gives information as to the conditions of the world of matter, the latter provides us with a knowledge of the processes in it. As the practical influencing of our surroundings in the direction of warding off injurious conditions, and fostering desirable ones, depends entirely upon the appropriate processes, a knowledge of these processes is absolutely indispensable, if conscious influence is to be effected; but this is just the aim of all science.

There are only two kinds of processes in our surroundings. On the one hand, alteration of the objects may be of such a kind that they appear to be essentially the same objects as before, while a few properties or relations have suffered change. This happens, for instance, when objects are moved in space, are warmed or cooled, or absorb or emit different kinds of light. On the other hand, the whole nature of the object may be changed as the result of the processes, as when water changes into ice, wine into vinegar, or air into nitric acid. Processes of the latter kind occur when two or more different objects are brought together under suitable conditions; but they can also be brought about in certain objects by the action of heat or of the electric current. The latter kind of processes is classed as belonging to Chemistry, while the others belong to Physics. The difference is, however, not a hard and fast one, and there is a fairly wide border region, which is usually dealt with by both Chemistry and by Physics. There is no disadvantage in this, for Science is a coherent whole; the division of it into sections is only an expression of the limited faculty of man, in consequence of which the knowledge and mastery of the whole of science by any one man has long been impossible. In recent times, scientific work in this border region has become so frequent and so important that it has developed into a special branch under the name of Physical, or better, General Chemistry. This book is intended to be an introduction to this subject. The name "General Chemistry" implies that it is concerned with the more general chemical properties and processes of matter, or in other words, with the more general natural laws relating to these properties and processes, rather than with the individual substances. The name "Physical Chemistry" indicates that much greater use is made of the manifold methods of Physics, than in descriptive or in preparative chemistry, which have hitherto formed the chief part of chemical science.

Weight.—The most general property, on the presence of which the conception of matter is made to depend, is weight. For example, the real image of an object projected by a concave mirror has no weight, and so is not called an object, although in other respects it appears to be material. Such a connexion of a name and an idea is arbitrary, and is purely a matter of convenience. It is convenient to limit our considerations to systems in which we recognise weight, and to call such systems, for the sake of brevity, objects.

Weight is directly recognised by the muscle-sense, since we feel a certain amount of effort in lifting things. It is soon evident that different things give rise to different effort; we say, then, they have different weights, or are heavier or lighter. This judgment is not very definite, and breaks down altogether when certain limits on either side are exceeded. If the body is so heavy that it cannot be lifted, the possibility of recognising difference in weight disappears. If it is very light, the impression on the muscles is so small that it is no longer possible to distinguish any difference. Further, different people will come to different conclusions as to the weight; a child will find a body very heavy which is light to an adult. The individual man varies so much in health and other respects that even his judgment of the weight of a body may vary.

All these circumstances greatly reduce the precision of the judgment which can be pronounced as to the weight of a body by lifting it. These differences are subjective, or dependent upon the person of the observer, and it is impossible by such a method to say what would be the state of affairs if these subjective differences could be avoided, and the objective condition of the body itself be alone considered. It is of essential importance that the latter be known, since it is the foundation of the former.

Measurement.—We obtain the objective value of the weight of a body when we measure it. Since all exact sciences rest upon the process of measuring, we shall consider it in its general aspect.

All measuring is a comparison of systems of the same kind. Lengths can only be measured with lengths, times with times, and weights, too, only with weights. All measuring begins with the arbitrary choice of a unit. We may choose any definite body and declare that its weight is to be the unit or the standard for all other weights.

After this has been done, any other body can be compared with this normal weight. To do so, we establish that the given body has a greater or less weight than, or the same weight as, the standard.

This can be approximately ascertained by lifting. If we call the arbitrarily chosen standard E and the body to be compared K, and if we lift first E and then K, it is often possible to say at once which of them requires the greater effort. This is because we have still a recollection of the effort required to lift E when we afterwards lift K. The sooner the second experiment follows the first, the more definite is this recollection. If the difference is so small that we are not quite certain of it, repetition of lifting E and K alternately will frequently enable us to recognise the existence of the difference by the consequent improvement of the recollection. If even then no difference is felt, the weights are said to be equal.

It is the general experience that when one person has found E to be heavier than K, all other persons will do the same. The only difference is that some people can recognise differences where others find equality. Summing up these experiences, we say that bodies are objectively heavier and lighter, corresponding to the results of concordant subjective estimates. Still, sensibility, or the ability to recognise small differences, is subjectively variable. All bodies can be arranged objectively in a series, which begins with the lightest and ends with the heaviest, although several bodies may have to be grouped together at the same place, because their weights are judged to be equal. Inability to form a judgment limits the series at both ends.

Measuring Instruments. — Although the subjective factor in measurement of weight has been, to some extent, excluded by the choice of a standard and by suitable arrangement of the experiment, there still remains the disadvantages of restricted range and of limited accuracy of measurement. There was no prospect of overcoming this disadvantage without some material change in human nature and ability; it was, therefore, a very great advance when both of these limits were considerably extended by the invention of Measuring Instruments.

The principle of all measuring instruments is that the object to be measured is allowed to act on a suitable system, which is influenced by it in some recognisable manner; the magnitude of the object is derived from the magnitude of this influence. The process was the same when direct use was made of the organs of sense, so that it really comes to be the substitution of the human organs of sense by some other system, which, like it, is also susceptible to change. For the rest, it will be found to have the characteristics already mentioned.

Consider, by way of illustration, a common letter scale (Fig. 1). When an object, whose weight is to be ascertained, is laid upon the pan, the loaded arm rotates, and remains in an oblique position. This angle of rotation corresponds to the muscular sensation of lifting, and by its means we can arrange the different bodies in the same order as before, beginning with the lightest. Here, too, there is a limit at each end, for too heavy bodies cannot be carried by the balance, and too light ones cause no recognisable movement; further, it depends on the sensibility of the balance whether two slightly different weights will be

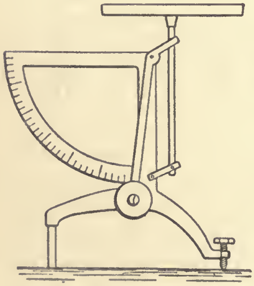

Fig. 1.

found to be the same or not. The main difference is that optical inspection of the angle of rotation on the attached scale is substituted for the muscular sensation.

But very considerable advantages have accrued from this substitution of the human body by an inanimate instrument. In the first place, the latter is less liable to change. Indeed, we rely so much (and rightly so) on its immutability that we provide it with a fixed scale, which expresses, once for all, the relation between weight and angle of rotation. The apparatus is thus possessed of an objective and unchangeable recollection, as it were, by means of which the continual use of the standard weight or of another weight is made unnecessary. In order to know whether a weighed body is lighter or heavier, all that is necessary is to determine once for all what scale division corresponds to the standard weight. In the second place, we can at will extend the limits in either direction. If we make the instrument very fine and light, we can measure very small weights with it; by strong and heavy construction it can be adapted to heavy loads. So that by division of the field of the function, and by appropriate construction of the instrument, the field can be extended at will, which, of course, cannot be done with the human body. Finally, by suitable refinement of the mechanism, the instrument can be made more sensitive, and that is only possible to a very limited extent (by practice) in the case of man.

Still, by these measures the disadvantages and limitations are only reduced, but not eliminated. The fineness of the construction of balances for the lightest weights, and the capacity for heavy weights has its technical limits, which are not absolutely fixed, but are only capable of finite extension as technique advances. So, too, the absolute sensibility, or the possibility of recognising small weights, is so much smaller the stronger and heavier the apparatus is, *i.e.* the greater the weight which it will carry. But the relative sensibility, measured by the fraction of the greatest weight which the balance will indicate, is so far independent of the size of the balance, and is practically defined by the fineness of the mechanical construction and the distinctness of the reading. There is a limit, however, at which the possibility of recognising any difference ceases. When no difference can be recognised the objects are said to be equal. Equality in a physical or experimental sense is therefore a relative term which depends upon the fineness or sensibility of the apparatus (organ of sense or instrument) which is employed to detect the difference.

The Lever Balance.—For scientific purposes another piece of apparatus, which depends on a different principle, is used instead of the instrument just described, in which the weights are shown by the different positions taken up by a pointer moving over a divided scale. In it, the effect of the weight upon a similarly movable apparatus is counterbalanced by allowing other weights to act upon the apparatus in the opposite direction. If these weights are known, their sum is equal to the unknown weight.

The advantage of this method is as follows. A balance constructed on the former principle, if it is to have a sufficient range, must not be too sensitive, or even a small weight will drive the pointer off the scale. But on the other principle the balance may be as sensitive as technical means will allow, since the movement of the pointer, which indicates when equilibrium is attained, need only be very small; all that is necessary to know is that when a certain weight is opposed to the unknown weight, the pointer remains in its original place, or oscillates equally on each side of it.

Methods which depend on this principle of neutralising or compensating the magnitude to be measured by another, equal to it but opposite in direction, and of arranging the instrument so that it will only indicate that this compensation has been effected, are known as Zero Methods. The name indicates that the effect to be measured has been reduced to zero in the manner described, and that this has been in fact accomplished. A much more accurate measurement is thus attained than with the other methods, in which an alteration proportional to the effect, or a "swing" corresponding to it, is obtained. The latter may be called Scale Methods in contrast with the zero methods; they have the merit of simplicity and rapidity, but these are gained at the expense of accuracy and sensibility.

The accuracy of a method is expressed by that fraction of the total value which is just recognisable; the sensibility by the absolute value of the smallest recognisable change in the magnitude to be measured.

The zero method is applied to the determination of weight by means of the Lever Balance and Sets of Weights. The former consists of a double lever with two equal arms, the lever resting upon a sharp, straight edge as its axis of rotation; from the ends of the beam are suspended the two scale-pans of equal weight, which also rest on knife edges parallel to the other knife edge. All three knife edges are in one plane. The apparatus is exactly symmetrical with respect to the middle axis, and the weight of the instrument is so distributed that the centre of gravity lies very little below it. Thus a small over-weight on one side causes a considerable rotation of the beam. The amount of this rotation remains practically constant when the pans are loaded with equal weights. It is thus possible to measure an unknown weight in the manner already described, by placing known weights upon the other pan, and changing them until the balance shows no excess weight on one side or the other. Figure 2 shows a balance such as is used for scientific purposes. The two-armed symmetrical beam is shown clearly; for lightness and rigidity it is built in the shape of an open triangular frame. The middle axis has its knife-edge on the under side, as the beam rests upon it; the two side knife-edges are on the upper side so as to carry the stirrups for the pans. The whole is enclosed in a glass case, for the instrument is so sensitive that it would be set in violent and irregular oscillation by accidental air currents in the room in which it is placed.

Absolute and Relative Weight.—One result of employing the zero method is that the real measuring apparatus in this case is the set of weights, *i.e.* the collection of known weights, by the combination of which any required weight (within the given limits) can be made up. The possibility of doing this depends upon certain laws relating to the weights of all objects, laws which are so well known that their validity is tacitly assumed whenever weighings are made, but which must, nevertheless, be explicitly stated in a scientific discussion of the subject.

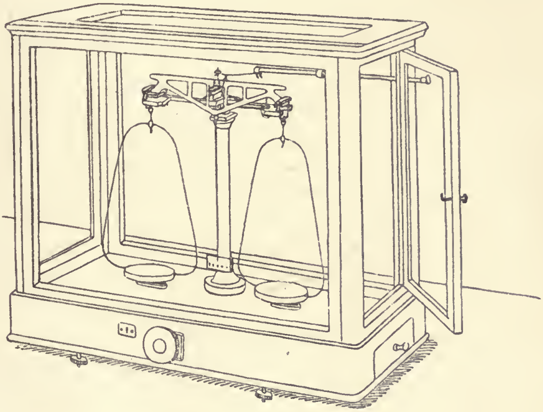

FIG. 2.

If two weights have been brought into equilibrium on a balance, equilibrium remains under all other circumstances, so long as the ratio of the arms of the balance remains the same. We know from other circumstances that the absolute weight of the object, or the force with which it is attracted to the earth, is by no means constant; it is less on a high mountain than in a valley, it also changes with the geographical latitude. But the ratio of absolute weights is never changed in these circumstances, whether the objects are composed of the same or of different material. The equilibrium remains independent of the change in absolute weight even in the case of two different weights which are brought into equilibrium by means of a balance with unequal arms. It follows, then, that different weights are changed by gravity to equal extents, or remain proportional to one another. For these weights, when in equilibrium, are inversely proportional to the arms of the lever on which they act; since the latter are not altered, the ratio of the weights must remain constant. The absolute weight of any object can, therefore, be represented by a product qg, in which q is a value depending solely on the object, and g denotes the value of gravity, which changes from place to place, but is independent of the nature of the object. The ratio of two absolute weights in any given place is given by the ratio $qg/q'g = q/q'$, whilst in some other place it is $qg'/q'g' = q/q'$, the same value as before.

The absolute weight qg must be carefully distinguished from the relative weight q. The former represents the force with which the object is attracted to the earth at any given place, and must be taken into account in considerations of force and work. The relative weight is, on the contrary, independent of the place; it would be the same on the sun's surface as on the earth. As many of the effects and properties of bodies, especially the quantity of work which they can give rise to during chemical changes, are proportional to the relative weight, it alone, as a rule, is of importance to chemists. Unless expressly stated otherwise, relative weight is meant when weight is referred to in this book.

Since on the ordinary lever balance unknown weights are determined by bringing them into equilibrium with known weights, only the ratio of different absolute weights is found, *i.e.* the relative weights are determined. In this sense, the balance is the characteristic instrument of the modern chemist.

The Unit of Weight.—As already mentioned, it is necessary to choose an object as standard of weight, and to refer all other weights to it. The first and most important requirement which such an object must satisfy is unchangeability. It should not lose particles by mechanical usage, or by evaporation; nor should it take up ponderable matter from the surrounding air. Easy of fulfilment as these conditions at first sight seem to be, it is in reality very difficult when it comes to the last degree of scientific accuracy. At present, a piece of metal made of platinum-iridium (the least changeable metal known), and preserved in Paris with the utmost care, serves as the standard; or rather, it represents a unit 1000 times its value, the reason being that, with our present means, the definition is more accurate with the larger than with the smaller piece. It is known as the kilogram standard, and the unit derived from it is the gram, abbreviated to g. From what has been said already regarding the laws of relative weight, this unit is evidently a sufficient standard, since it is independent of the place and of other variable conditions.

The Set of Weights.—Fractions and multiples of the unit are made in the following way. Two weights can be made equal by adding to or taking from the second until it is in equilibrium with the first one, as shown by an equal-armed balance. Now no balance is absolutely equal-armed, so the errors due to this must be avoided. This can be accomplished by bringing the standard weight into equilibrium with some other object, and then, having replaced the standard by the new weight, adjusting the latter until equilibrium is again attained. In this way the inequality of the arms does not matter, for it affects the two weights in the same manner, as they had been placed on the same scale-pan. This is known as weighing by substitution.

Any desired number of weights equivalent to the standard can be made in this way, and by putting them together any multiple of the unit. To make the fractions of the unit, *e.g.* the tenths, ten equal weights are made, the sum of which is approximately equal to the unit. The difference between the sum of these pieces and the unit is determined, and this divided by ten gives the alteration on each of the weights necessary to make them correct.

It may be urged that smaller weights must already be in use to determine this difference, but all that is needed is a number of equal, small weights, with which the difference can be determined; thus the problem can always be solved. When once the tenths, hundredths, etc., of the unit have been made approximately correct, the small deviations from the nominal value can be determined by comparison on the balance; and so a set of weights is obtained which is physically or numerically correct.

In reality every set of weights contains errors, *i.e.* small deviations of the single pieces from their nominal value. These errors are estimated in the way already described for the manufacture of the weights; the small difference between the real and the nominal value is found by bringing on to the scale-pan such combinations as have the same nominal value. For example, 2 is compared with 1 + 1, 5 with 2 + 2 + 1, etc. As many experimental equations are thus obtained as there are weights, and by solving the equations we obtain the true weights of the single pieces.

The practical details of this process are described in the Text-books of Experimental Physics or Chemistry.

Magnitude.—By a magnitude we understand a value for which the additive and commutative laws hold. By values we understand primarily such things as are similar among themselves and so form a class, but which differ in such a way that they can be definitely arranged in a series. Temperatures or degrees of heat have this property; they are so far alike that they all represent single conditions of heated bodies; they are different from one another in bringing the mercury of a thermometer to different positions. All these values form a definite series in which each value occurs once only and at a definite place. But temperatures are not magnitudes (at least not without further assumptions) since their parts do not admit of being arranged in any arbitrary order, but each temperature region has its well-defined place, as is most clearly shown by the figures on a thermometer scale.

On the other hand we recognise in the properties of weights, as already set forth, that we are dealing with magnitudes in the strictest sense. The use of a set of weights, and the control of its accuracy, depends on the fact that the individual pieces can be combined in any order and still give exactly the same sum, whatever the arrangement. The numerals as expressing measures are classed among such magnitudes; and have, too, been obtained by the combination of similar units. There cannot be the least doubt, therefore, that the standard of weight must be called one, and the weight which is treble the standard must be given the number of measure three. Magnitudes are measured by counting how many units are contained in them. Any other system (given the standard) is inadmissible as being liable to introduce errors in calculation. Temperatures, on the other hand, can be counted from any point we like; such as the melting-point of ice, which is the zero of the Réaumur and the Celsius scales; a different arbitrary starting-point for counting temperatures is the zero of the Fahrenheit thermometer, which lies 32° below the melting-point of ice.

It is of the utmost importance to have a clear conception of these questions, especially in the case of values which are in scientific use. The subject will be referred to again on a more suitable occasion.

The magnitudes to which weights belong have a special characteristic. The series of possible weights is unlimited only on one side; on the other it ends at zero. It resembles in this the series of positive numbers, which have the same property. There are no negative weights; they have no physical meaning. They would be weights which do not bring objects to the ground but away from it. The apparent exception in the case of the balloon, as is well known, depends on the buoyancy of the air; by itself, *i.e.* in a vacuum, it would fall to the ground.

When, at the end of the eighteenth century, the phenomena of combustion were explained by the escape of a hypothetical substance, phlogiston, from the combustible during the reaction, the objection was raised against this view (which in itself was quite consequent) that during combustion substances become heavier and not lighter. In order that the old view might be retained notwithstanding this, the further assumption was made that the weight of phlogiston was negative. But it was soon found necessary to abandon this expedient, as no substance with negative weight could be found. It might also have been said that such a substance would have long since escaped from the earth, since it would not only not be attracted to the earth, but be repelled from it. In this we have sufficient reason why substances with positive weight (*i.e.* attracted to the earth) alone are known on the earth, or are likely to be known.

The Conservation of Weight.—It is evident from the fact that the original kilogram kept in Paris has been used as the standard of weight throughout the whole world, and is intended to be so used in the future, that the belief is entertained that this weight has up to now remained unchanged, and will remain unchanged in the future. What grounds are there for this assumption?

The answer appears at first sight to be simple enough. Weighing from time to time will show whether the kilogram standard has remained unchanged, and thus prove its constancy.

But to weigh it again, use is made of another weight, and this must be assumed to have remained unchanged. If both have changed, weighing will only show the difference of the two changes. If by accident the two changes were equal, no difference could be recognised. Conversely, the absence of difference only admits of one conclusion, that the two have suffered the same change, which might possibly be zero. If, for example, some process within the earth's interior had changed the gravitation constant at a place, the balance would give not the slightest indication of it, for all weights would be affected in the same ratio, in accordance with the laws given on p. 8.

It has been found that different weights, carefully preserved, have not changed in relative weight in the course of time, no matter what the material was of which they were made. The simplest conclusion from this experience is that no change has occurred. This is practically the same as the previous conclusion, that all weights have been affected by changes in the same proportion, for the balance affords no means of distinguishing between the two. The cause of this is that the balance only gives relative weights, and therefore only the ratio of weights and not their absolute amounts. Other apparatus and measurements (pendulum measurements in particular) give information as to absolute weight; they show that the absolute weight at a given place remains constant, within the limits of error of the measurements. It is thus scientifically justifiable to assume complete constancy of relative weight.

This constancy of weight holds so far that complete change in the nature of the body, so long as there is no accession or departure of weighable substances, has no measurable effect on the weight. Attempts to find a difference in weight between water and ice prepared from it by freezing have been unsuccessful. No process of any kind is known by which the weight of a sealed-up body can be changed.

The most incisive changes in the nature of a body are chemical. Substances which can interact have been sealed up in glass vessels of such a shape that they are at first kept separate, and, after sealing up and weighing, are mixed by inverting the vessel, and thus caused to interact. Very careful weighings before and after the action appeared at first to show small differences, which were greater than the error of weighing. In consequence many people believed that chemical processes might be accompanied by a change of weight. In a final research, however, H. Landolt (1908) proved that they were experimental errors, mainly due to changes in the surface condition of the glass vessel brought about by the increased temperature during the reaction. When all the sources of error were allowed for, there remained no difference larger than the experimental error, and the law of the conservation of weight during a chemical process has been fully established so far as our present methods allow.

Historically this law has, in isolated cases, been regarded for centuries as correct. Its general validity was first stated by Lavoisier about the end of the eighteenth century, and experimentally verified in many cases. Lavoisier also pointed out the important applications of this law to chemical reactions. If, for instance, a substance changes weight during a reaction, the conclusion is justified that weighable substances have come to it or left it, according to the direction of the change in weight.

Work.—The general property of weight brings us to a very important and general idea, that of mechanical work or, shortly, work. To lift a heavy object from the ground and lay it on the table requires exertion, which is greater the greater the absolute weight of the object, and which also increases with the height through which the object is raised. This exertion, and what is at the bottom of it, has also the character of a magnitude in the strict sense, since it is commutatively additive. Two equally heavy objects require greater exertion if lifted together, and we may put it at double the exertion. The same is true of the height; to raise it twice the height would demand twice the exertion. The work is measured by the product of the weight and the height.

But these are only gross approximations with no claim to scientific accuracy, and the human body must be replaced by some form of apparatus specially devised for the purpose, just as in the determination of weight. A very simple contrivance will serve; for example, the two-armed lever, which has been already used in the balance.

If the lever has unequal arms, equilibrium results when the weights on the two arms are inversely proportional to their lengths. In Fig. 3 ACB is the lever; C is the axis. If a and b denote the lengths of the arms, and A, B the weights on them, then, according to the law that A and B are inversely proportional to a and b, A/B = b/a,

Fig. 3.

or Aa = Bb. To look a little closer into this equilibrium, suppose the lever to make a very small rotation. If this raises A a little, B must sink a little, and the two distances will be in the ratio of the lengths of the arms. For a very small rotation the arcs α and β may be considered as straight lines. From $\alpha/\beta = \mathrm{a}/\mathrm{b}$, and the former equation, we have $\mathrm{A}\alpha = \mathrm{B}\beta$ as the condition or definition of equilibrium. The products $\mathrm{A}\alpha$ and $\mathrm{B}\beta$ are the products of the absolute weights and the corresponding distances through which each of them has been displaced, *i.e.* they are the amounts of work; and for equilibrium, the "virtual" works must be equal. Virtual work is that which results from an infinitely small movement of the system.

What has just been said of the lever has been found to be a perfectly general law for all mechanical machines. By these is meant a combination of bodies such that the result of a certain movement at one place is a forced movement in some other place. The distances traversed stand in a definite ratio, which depends on the nature of the machine, and the law holds that machines of this kind are in equilibrium when the forces acting at the points in motion (and referred to the direction of motion) are opposed in direction, and are inversely proportional to the displacements. That is to say, the products of force and distance, or the quantities of work, are equal and opposite, *i.e.* if the one motion implies work in one direction, the other implies an equal amount of work in the opposite direction.

Work has one property in common with weight—it is a magnitude, for work can be experimentally summed by machines of this kind by allowing different forces to act on the same point. Since a force has a definite direction, attention must be paid to this, and the summation must be geometrical and not arithmetical. The clearest way is to represent the magnitudes and directions of the different forces by straight lines, and place these together; the lines joining the starting-point and the end point give the geometrical sum. Geometry shows that the law of commutation holds, for the end point is the same in whatever order the lines are put together.

Work is not an essentially positive magnitude like weight, but can occur in two opposed forms which subtract from each other instead of adding together. Consider any force, say a given weight, and consider its possible movements. They may be either risings or fallings. If the former, work is done upon the body; if the latter, work is performed by it. Work done is denoted as positive; work performed as negative. It is to be noticed that the result is reversed if the calculation is made for the surroundings instead of for the object, for it loses just as much work as the object takes up and *vice versa*.

The amounts of virtual work of a machine in equilibrium are therefore always of opposite sign, and as they are numerically equal, their sum is zero. The condition of mechanical equilibrium in any machine is that the sum of the virtual works must be zero.

The Conservation of Work.—If work is performed by means of a machine, the process consists in putting in work at one of its moveable points and taking it out at another. In the screw press, for example, work is expended on the handle of the spindle, and its rotation carries the screw further in its axis, and performs work in this direction. If the two are equal, the machine is in equilibrium; for it to move, the work applied must be greater than that taken out of it.

The question now arises how much greater it must be. It depends upon the perfection of the machine. The smaller the frictional resistance, the smaller will the requisite excess be, and with an ideally perfect machine with no friction it may be zero, in which case, however, the machine would move at an infinitely slow rate. In an ideal machine the work taken in is exactly equal to the work given out. But this is the condition of equilibrium; in order to calculate the maximum efficiency of a machine, it must be assumed to be in equilibrium, *i.e.* the work used up is equal to that gained. Under the most favourable conditions, a machine returns or retains the amount of work unchanged; it can never be increased by a machine. For if the work given out were greater than that supplied, the machine would simply go in the reverse direction. If, for example, a man raises a load by means of a pulley, and the work amounts to more than he can apply by the weight of his own body, the load will not be raised, but the body of the worker will rise.

This law that no machine can increase the quantity of work has been most searchingly tested during past ages. If it were not true, it would be possible to make a machine which could perform work without expense to the extent of the excess of work taken out over that put in. Innumerable inventors have sought in vain to contrive some such machine or perpetuum mobile, so that few scientific truths have been so thoroughly verified by experiment as that of the impossibility of creating work.

This result is by no means self-evident, for other magnitudes may be increased by machines; thus a given force can be magnified to any desired extent by means of an unequal-armed lever. Archimedes, the discoverer of part of the laws of levers, recognised this when he said that he could lift the world off its hinges, if he only had a fixed point to work on. He should have added that the movement would be infinitely small. For since the work applied would have been that of his muscles, the movement, according to the above law, would have been such that the product of it and the enormous load of the earth equalled the small amount of work at his disposal. The distance would have been vanishingly small, and there is nothing singular about it.

This law, that work cannot be increased by any machine, but in the most favourable case remains unchanged, is known as the law of the conservation of work. It is still incomplete, for the answer has not been given as to what becomes of the work when the machine gives out less than it takes in. We shall see later that a suitable extension of the idea of work brings this case also into line with the others.

The Conservation of Mass.—There is another property of matter which is proportional to the weight, and that is its mass. If p is the absolute weight and m the mass, $p = gm$, g being a proportionality factor, which changes in exactly the same manner as the factor g in the expression on p. 8 connecting absolute and relative weight. It has been found expedient to define weight and mass so that these two factors are identical, as has been already indicated by the use of the same letter g. The kilogram is thus the standard for mass as well as for relative weight.

The idea of mass is obtained from the properties which are brought into play when we attempt to set them in motion. If we again use muscular sensation as a rough measure for amounts of work, we recognise that more work is required to throw a large stone with a certain velocity than a small one. Similarly, it requires more work to communicate to a stone a great velocity than a small one. Without expenditure of work it cannot be set in motion at all, and this increases with the velocity on one hand, and on the other hand with the property which has been characterised above as a magnitude. The scientific name of this property is mass.

To compare two masses, equal velocities are imparted to them by the appropriate expenditure of work. By definition two objects have equal masses, if they require for this equal amounts of work. If two such masses are put together, twice the work must be imparted to the compound body to impart the same velocity. The masses are therefore additive, and it can be shown as before that the sum of a number of masses is independent of the order in which they are put together. Masses are magnitudes in the strict sense. The unit of mass is the mass of one gram.

Since the masses of objects are in a constant ratio to their relative weights, there is a law of the conservation of mass analogous to that of the conservation of weight. There is, in other words, no process known which changes an object or a system of objects in such a way that the system requires more or less work to impart to it the same velocity.

Kinetic Energy.—Since the connexion between mass and weight is frequently misunderstood, it will be discussed more thoroughly, especially as some of the considerations are important in other directions.

It was mentioned, in defining mass, that certain phenomena were observed when work was applied in order to set an object in motion. The converse also holds that bodies in motion can do work. We see how a pendulum in a complete swing first uses up work and gains motion, and then the motion falls off while the pendulum rises and therefore takes up work. An ideal pendulum always rises to the same height; the transformation of work into what for the sake of brevity is provisionally called motion, and the reverse transformation is therefore complete and in accord with the law of conservation, since the work is finally regained, although it has in the interval been transformed into something else.

This and every other thing which results from work and can be converted into work is in general called Energy. The particular kind of energy which is alternately changed into motion and retransformed into work is known as kinetic energy because the motion of the body concerned is characteristic of it. Still we shall soon learn that there are many other kinds of energy, all of which conform to the general definition: formation from work and transformation into work.

The kinetic energy of a body depends upon two factors as stated on p. 15; on the mass, and on the velocity of the body. If the same velocity is imparted to two equal masses, equal quantities of work are used up; the two masses moving together possess double the kinetic energy. Since the velocity has remained the same, and the mass has been doubled, the kinetic energy of a body in motion is proportional to its mass.

But such considerations do not tell us how much work is necessary to double the velocity of a given body. Experiments show that not double but four times the amount of work is required, and that in general the work necessary for imparting any given velocity is proportional to the square of the velocity. Kinetic energy is therefore proportional to the product of the mass and the square of the velocity. Regard must be paid to this particular mathematical form, as the first kind of energy, mechanical work, is a function of the first power of the force and of the distance, and is therefore proportional to the product of the two magnitudes. The factor $\frac{1}{2}$ has been introduced for special reasons as a proportionality factor for kinetic energy; kinetic energy is expressed by $E = \frac{1}{2}mc^2$, where c is the velocity. The same magnitude was called living force in earlier times, before the idea of energy had been developed. It is as well to know this name, in order to understand what is meant when we come across it, but it is not a good name, as it is a magnitude of a totally different nature from that of force as defined on p. 13.

Weight and Mass.—As is well known, the discovery of the laws of falling bodies by Galileo was, as it were, the threshold of modern science. A short discussion from the modern point of view will serve to elucidate the main features.

When a heavy body, whose absolute weight is p, falls through a distance s, it loses the work ps, and acquires a velocity $c = \sqrt{2gs}$, where g is the velocity at the end of the first second. This is the first part of Galileo's discovery; the second is that at any given place g is absolutely independent of the size and nature of the body (provided that secondary effects, such as the buoyancy and resistance of the air, are excluded). Since the kinetic energy $E = \frac{1}{2}mc^2$, we obtain, by substituting the above value of c, $E = mgs$. This is equal to the work ps, so that $ps = mgs$ or $p = mg$. From Galileo's second law g is the same for all bodies; thus the mass is proportional to the weight, and the two are in the same ratio for all substances. The ratio varies with the locality, since the velocity at the end of the first second varies with the gravity constant (p. 8). But the ratio of these two is constant, and, since from $p = mg$ we have $p/g = m$, the mass is constant or independent of the place. It is in this respect exactly like relative weight (p. 8), and has arbitrarily been taken as equal to the relative weight for all bodies, since the same objects have been used as the standard of mass and of relative weight (p. 8).

This simple relation between two totally different magnitudes is an important law of nature. It may be regarded as the cause of all bodies falling equally rapidly at any place. Different amounts of work, proportional to the weight, are required to raise them to the same height. But as the masses are proportional to the weight, these different amounts of work give rise to the same velocity, as the masses are measured (p. 15) by the work which is necessary to produce equal velocity in the objects considered.

Finally, we may enquire if any reason can be assigned for this strict proportionality between mass and weight. Newton proved that it really does exist by showing that the beat of pendulums, alike in form but constructed of different material and therefore differing in weight, was exactly the same. The beat of a pendulum is the expression of the time it takes to fall from its highest to its lowest position; and if the paths are made the same by making the pendulums of the same shape, and the beats are then found to be the same, it follows directly that all bodies fall with the same velocity through equal paths. Bessel (1826) reinvestigated the same subject with much more accurate means, and arrived at the same result, no differences being observed which exceeded the very small experimental error.

No satisfactory explanation of this important law has yet been suggested. All that can be said is that weight and mass must be united in all objects which remain on our globe. It has been mentioned already that a body without weight would soon betake itself into space. The following consideration shows that something similar would occur with a body without mass. If work is communicated to a body by impact, and is transformed into kinetic energy, the resulting velocity is given by $E = \frac{1}{2}mc^2$. The velocity is therefore greater the smaller the mass, and (for finite values of E) would become infinitely large if the mass became zero, *i.e.* the object would escape observation. The objects known to us must therefore possess both weight and mass; some further reason, as yet unknown, is required before the strict proportionality between them can be understood.

The Conservation of Energy.—A perpetuum mobile has been experimentally proved impossible both in the case of work and its mutual transformations, and also when kinetic energy is produced and is absorbed in the machine. The latter can never be actually excluded altogether, since the parts of the machine are always made of bodies which have mass, and must, with any finite velocity, take up corresponding amounts of kinetic energy.

The fact that even when the kinetic energy is taken into account, no work can be produced from nothing, necessarily leads to the following conclusions. If work is transformed into kinetic energy and this back into work, the work finally obtained can never be greater than the initial amount, otherwise a perpetuum mobile would be possible. It is generally smaller, but becomes more nearly the same the more perfect the machine; in the ideal machine both are equal. This is most simply expressed by saying that work in its transformation gives rise to an amount of kinetic energy equal to the work used up. Since the two magnitudes are measured independently of each other, and in quite different units, it is only a matter of definition: we call such quantities of the two kinds of energy equal which are formed by mutual transformation. To follow out this definition, the units have only to be so chosen that the same numerals come out in the two cases. How this is arranged will be explained soon.

If this definition and measurement are taken for granted, the law of the conservation of energy can be extended to the case where the work is not converted into work but into kinetic energy. The quantity of the latter is equal to the work which has disappeared, and the sum of the two remains constant. If A is the quantity of work and B the kinetic energy in an isolated purely mechanical system, the sum A + B is invariable, however great A or B may be at any moment. Our solar system is an example. If the earth is at a definite distance from the sun (which absolutely fixes its quantity of work), its kinetic energy has always the same value. It follows from this, since the earth's mass remains constant, that its velocity has always the same value, although it may be at different places in the path.

This relation is the law of the conservation of kinetic energy. It is a particular case of a much more general law, the law of the conservation of energy.

Other kinds of energy can be transformed into kinetic energy, and conversely, in just the same way as work. Since experience has shown the impossibility of a perpetuum mobile in the case of other kinds of energy, electrical energy, for instance, or the energy of living organisms, the same conclusion must be drawn with the suitable extension: in any isolated system the sum total of all the energy present is constant, however the various kinds of energy may change into each other. By an isolated system is meant, as usual, one in which no energy is taken up from without or lost from it. This law assumes, as explained above, that such amounts of the various kinds of energy are to be considered equal which result from their mutual transformation.

It is one of the most important laws in the whole of exact science. It was first proclaimed by Julius Robert Mayer in Heilbronn (1842); it was later independently discovered by Joule in Manchester, Colding in Copenhagen, and Helmholtz in Potsdam. Occasions of returning to particular applications of this law, which will make it more clearly understood, will frequently arise.

Units.—Since the selection and appropriate manipulation of units is of fundamental importance for the whole of the exact sciences, it may be well to arrange together those which will be made use of later.

First come time and space, which enter into all our experiences.

As to time, it is not a magnitude in the strict sense, for it is not additive in any order. On the contrary, time runs in such a manner that what has gone never returns, and an earlier time can never be kept and compared with a later time. This difficulty is overcome by defining equal times as those in which equal increments of a process, absolutely unaffected by external influences, are accomplished. We are now met with the difficulty of being certain whether a process is really unaffected, although no influences are known, and we have recourse to the same means as were applied in the case of the constancy of weights; different processes, which to the best of our knowledge are really unaffected, are compared with each other, until we are satisfied whether the definition can be consistently applied to them all.

The rotation of the earth on its axis is regarded as a process of this kind. It causes the sequence of day and night, and the mean value of the change is divided into 24 hours, and this into 60 minutes of 60 seconds each. A mean solar day is thus 86,400 seconds: the second is the scientific unit of time. The motion of the earth round the sun, which depends on other conditions and determines the year, is used as a control. The ratio of these two times has remained so constant during the historic ages that no deviations have been recognised, although the comparison can be made with very great accuracy. This definition of time has been found adequate to all the time phenomena in the earth and in the universe since numerous simple laws of nature have been discovered, the basis of which is this method of measuring time.

The immediate space unit is the unit of length, as defined by the length, at the temperature of melting ice, of a rod of platinum-iridium which is preserved in Paris. This is called a metre, abbreviated to m. The one-hundredth part of this length, the centimetre, cm., is used as scientific unit. The square and the cube with side of 1 centimetre are the derived units of area, and of space; they are the square centimetre, and cubic centimetre—written sq.cm. and cb.cm. or ccm.

As already explained, the unit of mass and what is numerically equal, relative weight, is the kilogram of platinum-iridium, likewise kept at Paris. Originally it was intended to be exactly the weight of 1 cubic decimetre of water at its maximum density (at 4° C.); but as two weights can be more accurately compared than this definition can be experimentally realised, the definition has been abandoned, and the piece of metal is taken as the standard of mass. By a fortunate accident the weight of a cubic decimetre of water was fairly accurately determined more than a century ago, for it is only 0·024 g. less than the platinum kilogram. In consequence, the volume of a kilogram of water can be regarded as equal to a cubic decimetre, or 1 ccm. as 1 g. of water.

These three fundamental units thus defined, a number of derived units can be given. The unit of velocity is the velocity when 1 cm. is traversed in 1 second; this unit is cm./sec. since the velocity is proportional to the distance and inversely proportional to the time.

The unit of energy is defined by means of these. Kinetic energy is used for this purpose; it (p. 16) depends on the units of mass and of velocity (*i.e.* length and time), since it is defined by the equation $B = \frac{1}{2}mc^2$. If $c = 1$, m $must = 2$, for B to remain $= 1$. The unit of energy is thus the kinetic energy possessed by a mass of 2 grams moving with a velocity of 1 centimetre per second. It is called the Erg, and is a very small unit. The unit of any other kind of energy is the amount of it which is obtained from 1 erg of kinetic energy.

For example, the unit of work is the work which a mass of 2g with a velocity of 1 cm./sec. can perform when it loses this velocity. On the other hand work is defined as the product of distance and force. The unit of length, 1 cm., has already been fixed, the unit of force is the force which acting through 1 cm. produces 1 erg. Since the erg is very small, this unit of force (the dyne) is also very small.

As an illustration of these definitions, we may calculate the force of gravity, *i.e.* the force which acts as weight on 1 gram. We make use of the well-known observation that when an object has fallen during 1 second, the distance traversed is 490 cm. and the velocity has become 980 cm./sec. The work is therefore 490g, where g is the unknown magnitude, and the kinetic energy is $\frac{1}{2} . 1 . 980^2$, since in the expression $\frac{1}{2}mc^2$, $m = 1$ and $c = 980$. From $490\ g = \frac{1}{2}980^2$, we get $g = 980$. The same value would be obtained from any other pair of corresponding figures. The force of gravity is thus 980 dynes. This is an approximate figure, for it has been explained already that gravity changes with the locality. The standard value for latitude 45° and sea-level is 980·53.

CHAPTER II

THE STATES OF AGGREGATION. GASES

Bodies and Substances.—The two laws of the conservation of weight and mass are true of all objects, and are therefore quite general. For this very reason they are of no use for the discrimination of individual objects. We must therefore look out for regularities which have a narrower field, in that they relate only to special groups or kinds of bodies, but which thereby bring us nearer to the final goal of science, a comprehension of the whole diversity of nature.

The specific properties of bodies, those which cannot be removed singly at will from the object with which they are associated, have been already described as those with which chemistry is concerned. Since a given body can be divided up at will, size and shape are not specific properties, although they characterise the particular body. Shape and size are accordingly left out of account and all bodies whose specific properties are the same are considered to be the same. The name substance has been introduced for this new idea.

The general fact that very often bodies different in size and shape have the same specific properties has been observed for a very long time. So old, that it has found universal expression in language which possesses a large number of names for definite substances, *i.e.* those with identical specific properties. Sugar is such a name. By it we distinguish bodies of widely different shape and size, if they have certain specific properties, such as solubility in water, sweet taste, transparency (or in the case of very small pieces the corresponding white colour), turning brown when heated, fermenting under the influence of yeast, etc. etc.

The importance of this process of scientific classification is clear if we reflect that all bodies which occur in the world can be imagined so arranged that all those with identical specific properties form a single class. These classes are obviously much less numerous than the single bodies, and the problem of descriptive science is extraordinarily curtailed because whatever is to be said about the specific properties is the same for all the single bodies of the class.

Here, too, the natural law holds that the simplicity and condensation obtained in this way are very far-reaching. The innumerable objects which make up the earth's surface, for instance, can be arranged in a few thousand classes of substances, and these minerals are so well known that it is considered a specially lucky accident for one to discover a new mineral. This arises from the fact that the different specific properties do not occur in all the possible combinations, but only in quite definite and isolated combinations. There are thus immeasurably fewer actual substances than could be imagined. This indeed is the reason why the untutored observation of early races had noticed this circumstance and fixed it in their languages.

Chemistry is thus directed to the problem of confirming by exact investigation this co-existence of definite properties, and bringing them, as far as possible, into scientific, *i.e.* regular, co-ordination. To this end all properties must be examined, a task which is inexhaustible, but the gradual accomplishment of which is being steadily achieved. We now enter into this work, and will consider in turn the most important and best-known properties.

The States of Aggregation.—The most obvious property, one which divides all substances into three great classes, is their state of aggregation. There is, as a rule, no doubt whether a given object before us is a solid, a liquid, or a gas. A body which retains its shape when handled is called a solid; one whose shape adapts itself to its surroundings (vessel), but retains its volume and appears to be bounded above by an even surface, is a liquid; and a body which possesses mass and weight, but no individual form or volume, but in both respects is dependent upon its surroundings, is called a gas.

There are bodies about which we may be in doubt as to which category they belong; their number is not large, however, and they in no way affect the appropriateness of this classification.

The question arises, how far this popular differentiation is of real scientific significance. Differences in colour for example are quite as striking to the eye as the differences of state. An attempt to construct classes of white, yellow, red, etc., substances will prove this classification to be ineffective and worthless. The reason is that a large number of other properties are associated with the state of aggregation, and practically no such connexion has ever been found in the case of colour. There is an empirical difference in value. We shall now proceed directly to a description of the three states of aggregation and their associated properties.

One other circumstance must be dealt with first. There are certain circumstances which are always present in the study of substances, and cannot be disregarded. They are not specific properties, as they can be changed at will; but they are values defining certain kinds of energy, which exist everywhere, and from which bodies cannot be removed. They are first and foremost, pressure and temperature. We live in a gaseous substance, the atmospheric air, in which there is a certain, somewhat variable pressure, called the atmospheric pressure. Temperature, too, is a property of heat, possessed by all bodies. It varies according to climate and season within moderately wide limits, which are, however, narrow in comparison with the range of artificial temperatures. The same is true with regard to changes of pressure. No body can be investigated independently of these two factors.

They have no effect on weight and mass, and were not mentioned in connexion with them. But, as practically all the specific properties of substances change with pressure and temperature, it is necessary to set forth in detail their behaviour. Their effect on bodies differs according to their state of aggregation. While the condition of gases is extensively changed by pressure and temperature, they have much less effect upon liquids, and less still on solids. They also bring about changes from one state to another; increase of temperature turns solids into liquids and liquids into gases; increase of pressure may liquefy gases. These are the simplest chemical transformations, and from this point of view, pressure and temperature have a special interest for us.

As both these notions have been scientifically developed in connexion with their effect on the states of aggregation, the historical sequence will be retained in what follows. This is, as a rule, expedient, for the natural development of science has always proceeded from the easier to the more difficult, a process equally well adapted for individual development. It is a recognised biological law that each individual organism follows in its physiological development the same way, in the main, that its species has proceeded along in its evolution from the simplest forms.

The Gas Law.—Matter in the gaseous state is distinguished by its capability of completely filling any given space as well as by its want of any definite form. In this state matter occupies more space than in any other, and obeys simpler laws.

A given mass of gas occupies a definite volume v only when it is at a definite temperature t and under a definite pressure p. In general we may put $v = f(p, t)$, where $f(p, t)$ signifies a function of p and t whose form is to be determined.

The influence of pressure is such that when the pressure increases the volume diminishes in the inverse ratio. This law was discovered by Robert Boyle (1662) and goes at present mostly under his name. On the Continent it was usually called until recently Mariotte's law, but this physicist published it only in 1679. The algebraic expression of the law is

$$v : v' = p' : p,$$

or

$$vp = v'p',$$

where v and p, v′ and p′ are two pairs of corresponding volumes and pressures which one and the same gas occupies at the same temperature. That is, at a given temperature the product of the pressure and volume of a quantity of gas remains constant.

The product has twice the value for twice the quantity of gas, and can be used as a measure of the quantity of a gas, independent of the volume or pressure, but not of the temperature.

This law holds for all gases, no matter what their chemical nature, from which we may conclude that the cause of the law is to be found in something which is likewise independent of the chemical nature of the gas, and is a property of their particular state of aggregation.

A similar independence is found in the influence of temperature on the volume of gases. The law which obtains here was discovered simultaneously (1802) by Gay-Lussac and Dalton, and is usually named after the former.[1] According to this law all gases expand in the same proportion for the same increase of temperature.

If we put the volume of a gas at the temperature of melting ice and under a definite pressure equal to unity, it will be 1·367 when the temperature rises to that of boiling water. This range of temperature is usually divided into 100 parts, which are so determined that for every part the same increase of volume (namely ·00367) occurs, and these grades of temperature are called centigrade degrees. They are reckoned from the melting-point of ice, upwards with the positive and downwards with the negative sign. The increase of volume per degree is according to definition the same for all gases, and amounts to ·00367 or $\frac{1}{273}$ of the volume at 0°; it is called the coefficient of expansion.

The algebraic expression for this relation is found in the following formula :—

$$v = v_0(1 + \alpha t),$$

where v is the volume at the temperature t°, v_0 that at 0°; α is the coefficient of expansion.

If we warm the gas without allowing it to expand, the pressure increases. This increase may be easily calculated from Boyle's law. Suppose the gas by heating to have expanded from v_0 to v, and afterwards to be compressed again to v_0 at the temperature t, then according to Boyle's law the pressure p_0 at 0° must be to the pressure p at t° inversely as the corresponding volumes, *i.e.*

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[1] In England it is also frequently called Charles's Law.—(Tr.)

$$p_0 : p = v_0 : v,$$

or

$$pv_0 = p_0v.$$

If this equation is combined with the former, we have

$$p = p_0(1 + \alpha t).$$

Thus at constant volume the pressure increases with the temperature in the same ratio as the volume does under constant pressure. The relative increase of pressure per degree, or the coefficient of pressure is consequently equal to the coefficient of expansion.

Lastly, if we allow both pressure and volume to change, their product, which at constant temperature is constant, varies with varying temperature in the same way as each of the factors would do separately if the other were constant. For this general case we have, therefore,

$$pv = p_0v_0(1 + \alpha t).$$

Graphic Representation.—These relations are made clearer by a method which we shall frequently have to employ, and may therefore be explained in detail here. The principle consists in representing the numerical values of any magnitude by means of straight lines of proportionate length. If the magnitudes are mutually dependent, or are functions of one another, this dependence is represented in the following manner.

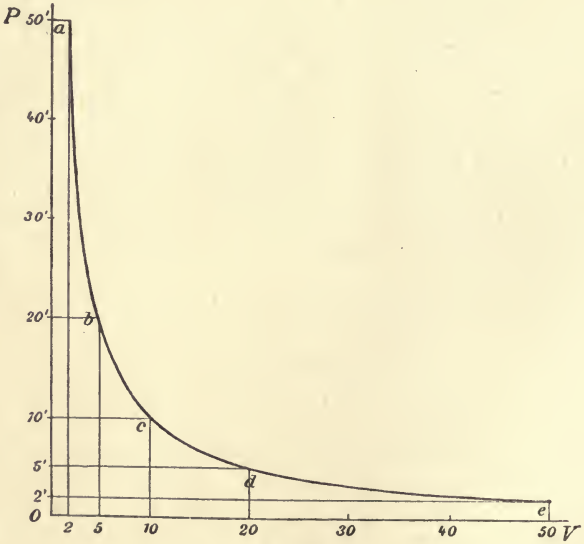

Fig. 4.

A value of the one magnitude is measured off on a horizontal straight line, starting from a fixed point O (Fig. 4), and a point is thus obtained, say 20. At this point a perpendicular is erected 20d, the length of which is a measure of the corresponding value of the other magnitude. In our case O20 might represent the volume of a given quantity of gas, and 20d the pressure. This condition of the gas is represented by d, and every other point in the plane of the diagram denotes some other condition, the pressure and volume for which can be read off in a similar way. The pressure corresponding to c is given by the length 10c and the volume by O10.

If now a quantity of gas which at 0° and a pressure of 20 cm. mercury has a volume of 5 ccm., the constant of Boyle's law is 100, and $pv = 100$. For a number of other arbitrarily chosen volumes the pressures are as follows:—

Volume	2	5	10	20	50 ccm.
Pressure	50	20	10	5	2 cm.

If these pairs of values are inserted in the diagram as already explained, the points a, b, c, d, e, are obtained. Obviously the same points would be obtained if the pressures were first plotted along OP and then the corresponding volumes measured towards the right.

If any number of pairs of values are added the points will lie between those given, and all possible pairs will form a series of points, which lie on a continuous curved line passing through a, b, c, d, e. The particular form of the curve obtained by applying Boyle's law is a rectangular hyperbola. It is thus a representation of Boyle's law as much as the equation $pv = \text{constant}$, and has the added advantage of clearness.

The line a, b, c, d, e, which represents the behaviour of the gas at constant temperature is an isothermal. The isothermals of gases, or the constant temperature curves, are rectangular hyperbolæ.

Such a system is called a co-ordinate system. The lines OP and OV, intersecting at the origin or zero point O, are the axes, and the lengths cut off the co-ordinates, horizontal co-ordinates being called the abscissae, and perpendicular ones ordinates. Every point has one ordinate and one abscissa, representing its distance from the corresponding axis, and is absolutely defined by values of these.

If negative values have to be plotted along with positive values, the axes are produced beyond O, positive values being reckoned to the right and above, negative values to the left and below. It is easily seen that this procedure conforms to the rules for calculation with negative values.

The products pv represent in the diagram the areas of the rectangles, bounded by the two axes and the co-ordinates, one corner of each of which lies in the curve. The latter has the property that all these rectangles, such as O2a50′, O5b20′, O10c10′, O20d5′, O50e2′ have the same area.

The isothermal for another temperature, *e.g.* 200°, is obtained by increasing all the volumes for the pressures plotted in the ratio $1:(1+\alpha t)$ in accordance with Gay-Lussac's law; in this case the ratio is 1 : 1·734. The preceding table now becomes:—

Pressure	2	5	10	20	50 cm.
Volume	86·70	34·68	17·34	8·670	3·468 ccm.

The curve is put in the same diagram; it is, of course, a rectangular hyperbola, since it satisfies a similar equation, $pv = 173{\cdot}4$; and consequently the rectangles enclosed by the axes and co-ordinates are equal in area.

From this it follows that any rectangle of the first curve is to any rectangle of the second curve in the ratio of $1:(1+\alpha t)$, which gives at once the usual form of the gas equation $pv = p_0v_0(1+\alpha t)$.

The Normal Condition.—This equation permits of the calculation of the volume which a gas would occupy at normal temperature and pressure when we know its volume at any given temperature t and pressure p. The standard values have been conventionally fixed so that the normal temperature is that of melting ice, or zero centigrade, and the normal pressure that of a column of mercury 76 cm. high, equal to a weight of 1033 g. per sq. cm.[1] For this purpose the equation is written in the form

$$v_0 = \frac{pv}{p_0(1+\alpha t)},$$

which is frequently employed in practice.

Absolute Temperatures.—We can give the gas equation $pv = p_0v_0(1+\alpha t)$ a simpler form by making use of the following consideration.

If the volumes of a gas at constant pressure and different temperatures are represented by lines oa, 100b (Fig. 5), drawn to the right, perpendicular to a vertical straight line corresponding to a thermometer scale, we obtain a straight line ab, which gives the volume for any other temperature. If this line is produced downwards, it will finally intersect the thermometer scale, *i.e.* there is a temperature at which the volume of a gas would become zero, provided that the law of expansion is still valid. Even if it is not, temperatures

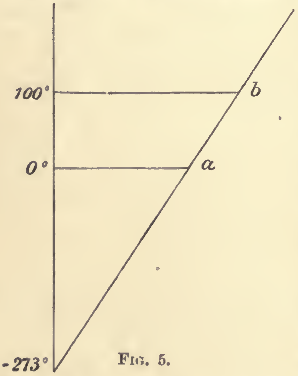

FIG. 5.

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[1] Mercury is 13·595 times heavier than water; a column 1 sq. cm. in section and 76 cm. high contains 76 ccm., and (as 1 ccm. water weighs 1 g.) weighs, therefore, 76 × 13·595 = 1033 g. For calculation into absolute units see p. 21.

can be counted from this point of intersection, and will have the advantage that the volumes of the gas are directly proportional to these new temperatures. The gas law will thus assume a simpler form.

A further important advantage is that temperature reckoned in this way is practically identical with a theoretical temperature scale based on general considerations of the properties of heat. This theoretical scale is independent of the nature of the thermometric substance, which is not the case with any other scale, the gas thermometer scale not excepted. The theoretical scale is, as a matter of fact, almost the same as that defined above.

This point of intersection is found as follows. The volume of a gas decreases ·00367 or 1/273 of its volume at 0° for every degree below 0°; at 273° below 0° (on the assumption that the law holds) the volume becomes zero. The zero of the new scale is therefore − 273° C., and every temperature has a numerical value greater by 273 than it has on the centigrade scale.

These temperatures are called absolute temperatures, and are denoted by T, in contrast with centigrade temperatures which are denoted by t. In numerical data, centigrade degrees have C added, absolute degrees have A placed after the figures.

The calculation is given by the following equations:—

$$pv = p_0v_0(1 + \alpha t) = p_0v_0(1 + t/273) = p_0v_0(273 + t)/273 = \frac{p_0v_0}{273}T,$$

since $T = 273 + t$. If finally the constant $p_0v_0/273$ is made equal to r, we obtain the simple and general expression

$$pv = rT.$$

The constant r is by its definition ($r = p_0v_0/273$) proportional to the quantity of gas. We shall find later that it is expedient to consider such quantities of different gases that r always has the same value. The new absolute constant arrived at by this means is denoted by R.

Volume Energy.—The product pv denotes an energy, for under given conditions, *e.g.* atmospheric pressure, the formation of a given quantity of gas can only occur if the pressure p is displaced or overcome through the space v, and this work is proportional to p, and to the space v occupied by the gas. To distinguish this form of energy from others, it is called Volume Energy. It belongs to the mechanical energies and is almost the only kind of mechanical energy which will enter into our future considerations.

It is not work in the ordinary sense, for that is the product of a force and a length, while here we have the product of a pressure and a volume. Nevertheless volume energy can easily be transformed into work, and conversely. In Fig. 6, A is a cylinder in which slides a frictionless piston K, actuated by a force, *e.g.* a weight G placed on it, the whole being placed in a vacuum. If now a gas is formed in the cylinder, and occupies the volume v, the piston must rise through the distance h, and takes up the work Gh, which has been performed by the gas in assuming the volume v at the pressure p, therefore $Gh = pv$. In equilibrium the two virtual works must be equal. Let the piston be raised by the small amount Δh, the work is $G\Delta h$, while the virtual change of volume energy is $p\Delta v$. If q is the cross-section of the cylinder, $\Delta v = q\Delta h$, and from $G\Delta h = p\Delta v = pq\Delta h$, we get $G = pq$ as the condition of equilibrium for this machine.

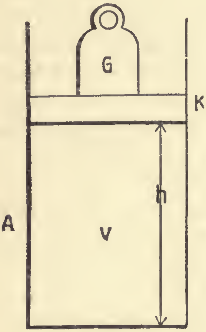

FIG. 6.

The form of the gas law $pv = rT$ indicates an important peculiarity of the volume energy of gases. At a given temperature T, the pressure under which a gas is formed has no effect on the volume energy used up in the process. For as the pressure becomes smaller, the volume increases, and the product of the two, which is the measure of the volume energy, remains constant. The gas laws can be stated as follows, and in this form certain peculiarities in the behaviour of gases is more readily intelligible: the volume energy required for the formation of a given quantity of gas is independent of the pressure and is proportional to the absolute temperature.

The circumstance that the left side of the equation $pv = rT$ denotes an energy, proves that rT must also denote a form of energy. As a matter of fact this magnitude is a particular form of energy, viz. heat. This will be returned to later.

As pv is an energy magnitude, it has, according to p. 20, an absolute value in ergs, and, in consequence, the absolute unit of pressure is that which acting through a volume of 1 cubic centimetre performs 1 erg of work.

This unit is related to the ordinary measurements of pressure as follows. One atmosphere of pressure is exerted by a column of mercury 76 cm. in height at sea level. As explained above, the work required to overcome this pressure by an increase of 1 ccm. in volume is equal to the work of raising a mercury column of 1 $cm.^2$ cross-section and 76 cm. height, through 1 cm. The action of gravity on a gram is 980 (more exactly 980·53) absolute units (p. 21), and as 1 ccm. of mercury weighs 13·5953 g., an atmosphere is $76 \times 980·53 \times 13·593 = 1013130$, *i.e.* a little over a million absolute units.

The change in the force of gravity with place has been taken into account, the value used being the normal value for latitude 45° and sea-level, viz. 980·53 units.

If the atmospheric pressure is to be expressed in weight units per square centimetre, this pressure is equal to the weight of a column of mercury of 1 sq. cm. cross-section and 76 cm. height, which amounts to 1033 g. This is so near to 1000 g. or a kilogram, that for technical purposes atmospheric pressure is often defined as a pressure of one kilogram per square centimetre; but for scientific use the above absolute definition is much to be preferred. If 75 cm. of mercury is taken as standard instead of 76 cm., the absolute pressure is rounded off to a million units under average conditions.

Pressure and Temperature.—Pressure and temperature are not magnitudes, since they are not truly additive. If two bodies of the same temperature are placed together, the resulting system has still the same temperature and not double that temperature; and the idea of a "doubled" temperature is not realisable. This is also expressed in common speech, for we speak of a higher or lower temperature, in figurative allusion to the spatial relations, but not of a larger or smaller temperature. It is nevertheless an ordered thing, for any temperature can be so arranged with others, that there is the same advance in the same direction from the first to the second, as from this to the third. All temperatures form a series, which is unidimensional, since there are no other differences between temperatures other than height.

Two temperatures which are equal to a third temperature are also equal to each other. A similar law holds for all magnitudes; it must be proved whether it also applies to values of the nature of temperatures, which we may call strengths or intensities. The proof is experimental of course; but we must first describe how temperatures are determined.

The thermometer, usually a vessel containing mercury, is used for this purpose. The vessel ends in a narrow tube, and the level of the mercury in this tube varies with the temperature. The reason is that heat enters the mercury and alters its condition; it rises, *i.e.* its volume is greater when heat enters it, and it falls when heat leaves it. If it does not move when placed in contact with another body, heat neither leaves nor enters it. This is the definition of equal temperatures, for when the mercury of the thermometer remains at rest, it is said to be at the same temperature as its surroundings.

In a similar way it can be shown that if the thermometer assumes the same level in contact with two different bodies, there will be no heat interchange when the two bodies are brought into direct contact; they are thermally unaffected. This is the experimental proof of the law, which, "self-evident" as it may seem, has very important consequences. It is, in fact, the foundation of the second law of the theory of heat.

The thermometer is thus a means of fixing temperatures so that they can be found again. Breakage of the thermometer would put an end to this, but, just as with the kilogram and the metre, a number of thermometers can be constructed as a precaution, and the identical temperatures marked on them. But there is a still better method. There are certain processes which take place at a quite definite temperature under easily reproduced conditions, so that these temperatures can be reproduced as often as necessary. The melting of pure ice is such a process, and by common consent the temperature of melting ice is chosen for one fixed point.

This, however, is not enough to establish a temperature scale. Consequently the boiling-point of pure water has been added as a second fixed point. It is appreciably affected by the variation of atmospheric pressure; but this influence is accurately known, and can be allowed for by taking the boiling point at normal pressure (p. 28) as the second fixed point.

In this way any number of fixed points could be established, were it not for technical difficulties. The question arises as to the subdivision of the temperature region between these two points. Indeed the distance covered by the mercury of the thermometer between these two temperatures may itself be regarded as such a division, but if the thermometer contains some other liquid instead of mercury, another division would be obtained, for the thermal expansions of liquids are by no means equal, and are not even proportional to one another.

Gases are not open to this objection; their expansion is independent of the nature of the gas, and is the same for all gases (p. 25). By a happy coincidence the expansion of mercury and of glass within moderate limits of temperature is so nearly proportional to that of gases that a mercury thermometer with a uniformly divided scale agrees pretty closely with the gas thermometer; the greatest difference between the two fixed points is only one or two tenths of a degree, according to the kind of glass.

It has been explained already (p. 28) how the absolute value of the expansion leads to a definition of a minimum point of temperature, the so-called absolute zero. No one has up to now succeeded in reaching this point, although recently it has been approached to within about 4°. It does not seem likely that it will be reached, as every degree in this vicinity adds enormously to the difficulty.

This process leads to a temperature series or scale, which may be taken to possess a definite general significance; but it must not be supposed that temperatures are divided by this scale into "equally large" portions, for the idea of magnitude is not applicable at all. As will be seen later, it is possible to make a temperature scale which is quite independent of the nature of the substance. It is based on the transformation of heat into work, and contains an arbitrary definition, which, however, is of very great generality. This "thermodynamic" scale is essentially the same as the gas scale.

Pressure is similar in nature to temperature, *i.e.* it is an intensity and not a magnitude. This is easily recognised if we recollect that two bodies at the same pressure remain at that pressure when put together. In this case speech is not quite so exact as in regard to temperature, for it is customary to speak of great and small pressures as well as of higher and lower pressures. This is because a zero point of pressure is easily fixed, and an evenly divided scale obtained under easily understood conditions.

The accessibility of the zero of pressure is connected with the fact that there are both positive and negative pressures, viz. those which tend to enlarge the volume as well as those which diminish it. Negative pressures occur, for example, in extended solids and in extended liquids (which are difficult to prepare). A rational scale, which, like the rational temperature scale, is based on the transformation into work, is obtained by the aid of the hydrostatic pressure of liquids, which depends on the application of gravity. The pressure is made proportional to the height of liquid, because the formation of a corresponding column of liquid requires an amount of work which is also proportional to the height.

In conclusion, it is readily seen that two pressures, which are equal to a third pressure, are also equal to each other. If they were not, it would be easy to make a perpetuum mobile by alternating the combinations of pressures. This mode of discussion will be frequently employed in other cases, and may be more fully explained at once.

Perpetuum Mobile of the Second Kind.—Consider a system, consisting of an infinitely large pressure reservoir B, and two smaller pressure machines (cylinders and pistons, cp. p. 30) A and C, the whole being in equilibrium as regards pressure. The cylinders are in equilibrium with B, being placed in contact with it. If A and C, which were not in direct union, were not in equilibrium under these conditions when they were joined together, work could be communicated to the one by the other. A is then brought into contact with C until their pressures are equalised, and work is set free. But now neither A nor C is in equilibrium with B; if A has given up work, its pressure must have become smaller than that of B, and the pressure of C must have become greater. When they are again connected with B, each of them will afford work, and in so doing they will return to their original condition. The series of processes can be repeated as often as desired.

If, therefore, the law was not true that two pressures which are equal to a third pressure are also equal to each other, a perpetuum mobile would be possible. But this has proved experimentally unattainable; the law must therefore be correct.

A perpetuum mobile of this kind would not necessarily imply the gain of work from nothing (for the work in the above arrangement could be regarded as derived from the heat store of B), but it would imply that a system in equilibrium could spontaneously set itself (*i.e.* without external influences) in motion or action. This, too, is a general experience, that what is in equilibrium will remain so. A perpetuum mobile which is not in contradiction to the law of conservation of energy, but does infringe this experimental law, is known as a perpetuum mobile of the second kind. The impossibility of this is just as important as the impossibility of a perpetuum mobile of the first kind, so far as definite laws are concerned; while the latter is the foundation of the first law of energetics, the former is the foundation of the second law—applications of which we shall frequently come across.

The Gas Law as a Limiting Case.—The gas law $pv = rT$ differs in nature from the laws of conservation previously mentioned. There are no known exceptions to the latter, while no gas is known which exactly obeys the gas law. The cause is to be found in the difference between the magnitudes concerned. There is no known means of affecting in the slightest degree the weight or mass of the substances concerned, but the space occupied by a gas depends on other circumstances beside pressure and temperature. In particular, the nature of the gas has an effect, which under ordinary conditions is small, but becomes more apparent the smaller the volume in which the gas is confined.

The formula $pv = rT$ is thus only a limiting law, *i.e.* a formula which in the main expresses the actual behaviour, but always with a small residual difference. This residue is smaller the smaller the pressure and the higher the temperature; but the behaviour of a real gas never realises the formula. An imaginary gas, which would obey this formula (and some others which will be mentioned later) exactly, is called an ideal gas. The behaviour of a real gas approaches an ideal gas more closely at high temperatures and low pressures.

CHAPTER III

THE SPECIFIC HEAT OF GASES AND THE FIRST LAW OF ENERGETICS

The Conservation of Heat.—The first quantitative investigations of thermal phenomena led to the establishment of a law of conservation in the form that heat may change in place but not in amount when bodies of different temperature are brought together. If the heat contained in a body is taken as proportional to its weight and its temperature, the temperatures calculated on the basis of this law agree perfectly with the temperatures experimentally found when various amounts of a substance at different temperatures are mixed together. If m_1 is the weight of one portion, and t_1 its temperature, and if m_2, t_2 are the corresponding values for the other portion, the mean temperature t after mixture is found by putting the gain of the one $m_1(t-t_1)$ equal to the loss of the other $m_2(t_2-t)$. This requirement, that the total quantity of heat remains constant, gives the equation $m_1(t-t_1)=m_2(t_2-t)$, hence $t=(m_1t_1+m_2t_2)/(m_1+m_2)$.

Specific Heat.—This equation is no longer valid when bodies of different nature are mixed if the amounts of each are simply taken as their weights. Agreement is restored, however, if every substance is measured in a special unit of weight; these different amounts of different substances behave, so far as heat exchange is concerned, like equal amounts of the same substance. The weights of substances must be multiplied by a specific factor to make them thermally equivalent. If these factors are c_1 and c_2 the equation becomes $m_1c_1(t-t_1)=m_2c_2(t_2-t)$. One c can be arbitrarily fixed and the actual relations will be represented by suitable determination of the other value.

These factors are the specific heats of substances. The specific heat of water is fixed as unity, and the equation becomes $m_1c_1(t-t_1)=m_0(t_0-t)$ or $c=m_0(t_0-t)/m_1(t-t_1)$, the substance with the sign $_0$ affixed being water. This equation is used in the determination of specific heats.

It should be observed that the zero of the temperature scale has no effect, since only differences of temperature appear in the formula, and they are independent of the zero.

These considerations assume that an absolute temperature scale is known (*i.e.* one independent of the nature of any definite substance), and that specific heats do not change with temperature. As for the first point, the scale of the gas thermometer (p. 32) agrees so closely with the absolute scale, that the one may be provisionally substituted for the other. Specific heats do generally vary with the temperature, but usually not to so large an extent as to materially modify the scheme given above.

The adoption of the specific heat of water as unity defines at the same time the unit of heat: it is the quantity of heat which is required to raise the temperature of one gram of water one degree. It is called the calorie and is denoted by c. or cal. This gives us another definition of specific heat: it is the amount of heat in calories which will raise the temperature of one gram of the substance one degree. Or more generally: the specific heat is the ratio between the amount of heat and the rise of temperature, referred to the unit of weight. Calling the first dW, the latter dt, and the weight of the body[1] m, its specific heat is $c = dW/mdt$.

In our subsequent considerations the amount of heat will not be referred to the gram but to quantity of the substance defined in a different way. The name heat capacity will be applied to the product of this new specific heat and weight. The definition of this magnitude is simply the ratio of the amount of heat supplied to the change of temperature, $k = dW/dt$; it always gives an indication of the quantity of substance meant as above.

Specific Heat of Gases.—These conceptions and explanations have been found generally applicable in the case of solids and liquids, but when they are extended to gases the law of the conservation of heat is no longer tenable in this simple form. This is very similar to what we found for the law of the conservation of work. There deviations occurred because part of the work was transformed into heat (because of friction) and therefore eludes measurement, and here a measurable fraction of the heat is converted into work and is lost to measurement.

The apparent contradiction which is met in attempting to apply the conception of specific heat, $c = \frac{dW}{dt}$, to gases is as follows. The overcoming of this difficulty led the way to the general law of the conservation of energy (p. 18).

The specific heat of air is found to be equal to 0·2375 when the experiment is so conducted that air is warmed to a definite

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[1] In higher mathematics infinitesimal changes are characterised by prefixing the letter d; this will be frequently employed in this book.

temperature higher than that of the liquid in a calorimeter, to which it is then made to give up the excess of heat, being all the time under the same pressure.

If, on the other hand, air is enclosed in a rigid vessel, only 0·1683 cal. are required to heat 1 g. one degree; its specific heat is much smaller than before.

By allowing the volume of the air to change, we can cause any desired temperature change to take place without supplying any heat, since cooling takes place on expansion, and heating in compression. The specific heat can thus be varied from $-\infty$ to $+\infty$.

On the other hand, Gay-Lussac (1807) made this experiment. Air was compressed in a hollow sphere, while another similar sphere was exhausted by the air-pump. When the two spheres were placed in the water of a calorimeter, and then connected with each other so that the compressed air could expand into the vacuum, no change in the temperature of the calorimeter took place. The change of volume alone, therefore, does not cause the change of temperature.

J. R. Mayer in 1842 reconciled these two apparently contradictory facts. To the questions: Whence comes the heat generated on the compression of a gas, and what becomes of the heat which vanishes when a gas expands? he gave the answer: The work that is done during the compression is changed into heat, and the work that the gas does in moving back the external air pressing upon it cannot spring into existence from nothing, but comes from the heat which the gas loses. If there is no external pressure to overcome, as in Gay-Lussac's experiment, there is no work to be done and consequently no heat is used up.

The possibility of calculating the ratio of heat to work (each measured in its appropriate manner) in their mutual transformation arises from these facts. It was accomplished as follows by J. R. Mayer (1842), who was the first to estimate this important number.

The specific heat of air at constant pressure, *i.e.* when at liberty to expand on being heated, is 0·2375. In other words, 1 g. of air is warmed 1° by 0·2375 cal., the air expanding and performing external work which can be calculated as follows. The volume of 1 g. of air at 0° is 773·3 ccm. at atmospheric pressure. At 1° the volume is $\frac{1}{273}$ greater, *i.e.* 2·830 ccm. greater, and the product of this and the pressure is the work performed. In absolute units atmospheric pressure is 1013130; the work is accordingly $2{\cdot}830 \times 1013130 = 2{\cdot}866 \times 10^6$ erg.

The specific heat at constant volume, *i.e.* without doing external work, has been found to be 0·1683. Addition of 0·1683 cal. warms 1 g. of air 1°. The difference of these values is equivalent to the work as calculated above, as neither external heat nor work has been evolved or used up. There is, however, this difference: in the first experiment, apart from the performance of external work, the volume has increased, while in the second it remained constant.

This makes no difference; for, according to Gay-Lussac's experiment (p. 37), mere expansion without doing work does not alter the temperature. If the heating under constant pressure is imagined to be followed by an increase of volume of 2·830 ccm. without any external work being done, 0·1683 cal. is sufficient for this change; from which it is seen that the difference must be set down as equal to the work performed.

This difference, $0{\cdot}2375 - 0{\cdot}1683 = 0{\cdot}0692$ cal., is equivalent to $2{\cdot}866 \times 10^6$ erg. This makes 1 cal $= 4{\cdot}144 \times 10^7$ erg; this is the mechanical equivalent of heat.

Mayer expressly stated that there are many kinds of "force," *i.e.* energy, for which the same relation holds as this in the case of gases, where the work done in changing the volume is proportional to the heat generated. But he made no further experiments on the subject; for these we are indebted to Joule (1843), whose work was continued through many years, and who first established the connexion between heat and the work of falling weights. The work is given by the product of the weight and the height, if the work, instead of being converted into kinetic energy, is transformed into heat by friction, so that the falling object has zero velocity at the end. Now Joule used the work of such weights to rub two iron plates, immersed in water, against each other. As these experience no permanent change, the work expended is transformed into heat, the quantity of which may be calculated from the mass and rise of temperature of the water. If we now put this quantity of heat equal to the work expended, we obtain, as Joule found, a perfectly constant ratio between them, which depends neither on the mode of changing the work into heat nor on any other condition of the experiments. The mean value of the ratio from frequently repeated determinations is

$$1 \text{ calorie} = 42660 \text{ g.cm.},$$

i.e. when the product of weight and height amounts to 42660, then 1 g. of water is warmed 1° C. by this amount of work. As gravity is 980·53 dynes, this number becomes, in absolute units, $4{\cdot}183 \times 10^7$ erg. It is more accurate than the value given above, because the measurements are capable of greater accuracy; the agreement is as close as could be looked for, considering the accuracy of the data used.

Absolute Units.—In absolute units one calorie is $4{\cdot}183 \times 10^7$ erg.

As the specific heat of water varies a little with temperature, the increase of temperature of a given quantity of water by the same amount of work will vary with the temperature. Rowland (1879) has experimentally proved this by direct experiments, and the above value refers to the mean temperature of 18°.

It is obvious that the unit of heat used above, the calorie, is arbitrary and unsystematic from the point of view of energetics. For as forms of mechanical energy and their factors are all so defined that they all have the same unit, the erg, the recognition of heat as a form of energy necessitates the selection of the same unit for it too. But this has not yet been adopted in scientific literature; to facilitate its introduction, all heat data in this book will be given in ergs.

It must be admitted that this unit is much too small for most measurements and calculations. The megerg would be convenient; a practical unit of 10^7 erg has come into use in electricity under the name Joule, abbreviated to j, and this unit has been adopted for practical use in this book. A calorie has thus the value of 4·183 joule, and we have the equations:

$$1 \text{ cal} = 4{\cdot}183 \text{ j, and } 1\text{j} = 0{\cdot}2391 \text{ cal.}$$

In addition to this, a unit one thousand times its value will also be employed, the kilojoule, denoted by kj. Thus

$$1 \text{ cal} = 0{\cdot}004183 \text{ kj, and } 1\text{kj} = 239{\cdot}1 \text{ cal} = 10^{10} \text{ erg.}$$

Isothermal Work of a Gas.—It is of importance for many purposes to know what work a gas can do when it expands at a constant temperature. In general (p. 30) this work will be expressed by the product of the pressure and the change of volume, pdv (where dv is the change of volume); the calculation presents some difficulties when the pressure is not constant. It is convenient for this purpose to represent the relation between the pressure and volume of gases graphically, by tabulating the pressures on a perpendicular straight line and the volumes on a horizontal one (p. 26). The curve bb obtained has the property that the product of the coordinates of any point is constant—corresponding to the gas equation pv = rT. Analytical geometry teaches us that the form of this curve is that of the rectangular hyperbola.

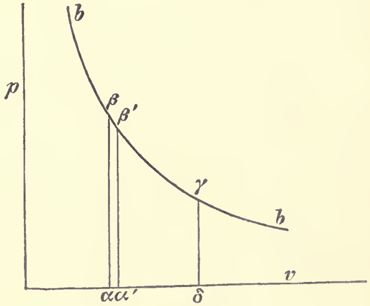

Fig. 7.

The work that is done when the volume changes by dv, *i.e.* the product p . dv, appears in Fig. 7 as a narrow quadrilateral surface $\alpha\alpha'\beta'\beta$. The total work performed on expansion between two states of the gas β and γ is therefore the sum of all the narrow quadrilaterals pdv, and thus equal to the quadrilateral $\alpha\beta\gamma\delta$. The calculation results, therefore, in the so-called quadrature of the hyperbola.

This problem cannot be solved by elementary mathematics; we must therefore be content with the general result. If a given quantity of gas represented by the gas constant r (p. 29) expands at the temperature T from the volume v_1 to the volume v_2, always exercising meanwhile the pressure given by the equation $pv = rT$, then the corresponding work has the value (since $v_2/v_1 = p_1/p_2$)

$$A = rT\lg\frac{v_2}{v_1} = rT\lg\frac{p_1}{p_2}.$$

Here lg stands for the natural logarithm, *i.e.* a logarithm to the base $e = 2{\cdot}71828$. The natural may be obtained from the ordinary or decimal logarithms by multiplying the latter by 2·30259.

Specific Heats at Constant Volume and at Constant Pressure.—Returning now to the question of the specific heats of gases, we see that we can only speak of such when we accurately determine what external work is done, if any. The simplest case would evidently be that where external work was altogether avoided; for example, where the gas was enclosed in an unyielding vessel and the specific heat determined under these circumstances. Unfortunately this theoretically most simple case has hitherto been experimentally quite impracticable, for the vessel in which the gas must be enclosed, and which necessarily takes part in the heating and cooling, has to be made so massive in order to resist the pressure called forth by the change of temperature, that it is responsible for by far the greater part of the heat-exchange, so that the part left for the gas is a very small fraction of the whole. Still, Joly (1890) succeeded in surmounting this difficulty by means of an ingenious differential method, and obtained results in close agreement with those obtained by the indirect method to be described below.

Such determinations are therefore conducted so that the changes of temperature take place under constant external pressure. In this way we obtain the specific heat at constant pressure, which we shall call c_p. Extensive experiments for the determination of this number have been made by Regnault, whose results will be given later. E. Wiedemann repeated some of them with simpler apparatus, and investigated the changes which the specific heat of many gases, especially those containing carbon, undergo with change of temperature.

To ascertain from these numbers the specific heat at constant volume c_v, the thermal equivalent of the external work has to be subtracted. The calculation is simplest when equal volumes of the different gases are considered. For reasons which will be explained later the volume which 32 g. of oxygen occupies under normal conditions (p. 28), is chosen. This volume is 22412 ccm. The expansion per degree is $\frac{22412}{273}$ ccm.

The work is obtained from this by multiplication by the normal pressure of 76 cm. mercury, $1{\cdot}01313 \times 10^6$ in absolute units, and thus amounts to $\frac{22412 \times 1013130}{273} = 8{\cdot}316 \times 10^7$ erg. If v_0 denotes the normal volume and p_0 the normal pressure, the work is given by $\frac{p_0 v_0}{273}$, which is equal to the gas constant r, since, in $r = \frac{p_0 v_0}{T_0}$, T_0 the temperature of melting ice is 273° on the absolute scale. The quantity of a gas which has the volume of 22412 ccm. under normal conditions is called a mol, and for these quantities the gas constant has the same value $8{\cdot}316 \times 10^7$ erg or 8·316j, and is denoted by R. If the specific heat at constant pressure, C_p, of a mol of gas (the molar heat) is known in joules, the molar heat at constant volume C_v is obtained by subtracting 8·316j:

$$C_v = C_p - R.$$

Molar heats are generally given in calories per degree. The value of R is then to be divided by 4·183, the amount of a calorie in joules, which gives $R = 1{\cdot}986$. The molar heat at constant pressure is 1·986 cal. per degree greater than at constant volume.

The numerical values of the heat capacities of gases depend on the nature of the gas, and will be dealt with when the connexion between physical and chemical properties is discussed. A few general statements will suffice for the present.

The molar heat of gases which are nearest the ideal gases (helium and its analogues) is 20·8 at constant pressure, and 12·2 at constant volume. It is independent of the temperature and is the smallest value observed for gases. For other gases it is greater and varies with temperature to a greater extent, the greater the value is. The independence of specific heat of the temperature is one of the characteristics of a perfect gas.

Density and Volume of Gases.—The density of a substance is the ratio of its relative weight or mass to the volume which it occupies. As the two former are numerically expressed by the weight of the object in grams, and the volume unit of water, one cubic centimetre weighs 1 g., the density can be expressed as the ratio of the weights of equal volumes of the substance and of pure water at 4°.

This is not very convenient, so far as gases are concerned. In the first place the numbers obtained are very small, since gases are hundreds or a thousand times lighter than equal volumes of water; and, further, the weight of unit volume of a gas varies to a high degree with temperature and pressure. The density must therefore be determined for the "normal condition" of gases at 0° and atmospheric pressure.

Under these conditions, the density of atmospheric air of average composition is 0·001293. A litre of air weighs a little over 5/4 g.

Air is too variable for a scientific standard, as it is not a pure substance with definite properties. Oxygen is the most suitable standard; its density is 0·001429.

The specific volume is the reciprocal of the density, *i.e.* the volume of one gram. For oxygen it is 699·8 ccm., almost exactly 700 ccm.

For other temperatures and pressures (in cm. of mercury) the weight of 1 ccm. of oxygen is

$$G = 0{\cdot}001429 \frac{p}{76(1 + \alpha t)},$$

and the volume of 1 g. of oxygen is

$$V = 699{\cdot}8 \frac{76(1 + \alpha t)}{p}.$$

To avoid the inconvenience mentioned above, it has become the practice to give, instead of the absolute density, the ratio of the weight of the gas in question to the weight of the normal gas, when both are at the same pressure and temperature. As these factors are the same for all gases, this ratio is independent of the pressure and temperature.

Molar Weight.—Air was formerly employed as a standard gas, but is not suitable for the reasons given. Oxygen has taken its place, but for reasons which will be explained later, oxygen is not used directly as a normal gas, but an imaginary gas whose density is $\frac{1}{32}$ that of oxygen. The weight of one cubic centimetre of the normal gas is 32 times as small as that of oxygen and is $0{\cdot}00004466p/76(1 + \alpha t)$. The relative density of oxygen thus becomes 32. As the densities of air and oxygen are in the ratio 0·001293/0·001429, densities referred to this normal gas are $32 \times 0{\cdot}001293/0{\cdot}001429 = 28{\cdot}98$ times as large as densities referred to air. It is important to remember this factor 28·98, as the latter densities are frequently given in the literature.

Densities referred to this normal gas are called the molecular weights of the gases, this nomenclature being based on the molecular hypothesis. To avoid the disadvantage of giving a name derived from a hypothesis to an empirical magnitude which is absolutely independent of any hypothesis, this name will be replaced for the present by the term molar weight.

Measurement of the Density of Gases.—The knowledge of the molar weights of different gases has a special interest for the chemist, and different methods of arriving at it have been contrived.

These all come in the end to the same thing, viz. both the volume and the weight of a given quantity of gas are determined at a definite temperature and pressure. If we then calculate how much an equal volume of the standard gas weighs under the same conditions, the ratio of the two weights gives the specific gravity required. If W is the weight of V volumes of the gas to be investigated at the temperature t and the pressure P, that of an equal volume of the normal gas is

$$g = \cdot 00004466 \frac{PV}{76(1 + \cdot 00367t)},$$

and the molar weight required, $m = \frac{W}{g}$, has the value

$$m = \frac{W \times 76(1 + \cdot 00367t)}{\cdot 00004466\ PV} = 6238 \frac{WT}{PV},$$

where $T = 273 + t$.

This equation holds for all methods of determining vapour densities; its application presupposes that the pressures are measured in centimetres of mercury, the volumes in cubic centimetres, the weights in grams, and the temperatures in centigrade degrees + 273. The various methods differ only in the means adopted to get a knowledge of these four requisite numbers.

If it is required to get as accurate determinations as possible of the density of gases that can be investigated at comparatively low temperatures, two equal glass globes of suitable size are employed; these can be closed by means of stop-cocks, and are exactly equalised as regards their weight and external volume. One of the globes is closed (preferably when exhausted) and this then serves as a counterpoise to the other, which is weighed alternately empty and filled with the gas whose density is to be determined. The counterpoise of equal external volume is rendered necessary by the fact that the total upward pressure exercised on the globes by the air in which they are weighed is about as great as the weight of the gas itself, and that this pressure is variable with the condition of the atmosphere. If, however, the variations affect both sides of the balance equally, as they do in the arrangement described, they have no influence on the result of the weighing. When the globe is weighed exhausted of air its volume is rendered somewhat smaller by the external atmospheric pressure, and consequently the upward pressure is also smaller, so that in very exact measurements this circumstance must be taken into account.

The difficulties encountered in such experiments lie in the necessity of weighing the large gas receptacles with great accuracy; the determination of the pressure, volume, and temperature can be made with sufficient exactness much more easily. In consequence of this we may frequently attain the desired end more conveniently and with greater precision by weighing the gas, not as a gas, but in the solid or liquid state. This by no means presupposes that the gas as such may be conveniently brought into this state (though this can usually be easily done with the aid of the low temperature of liquid air); we can make use of this mode of procedure whenever the gas can be generated from solid or liquid compounds, or can be converted into these. For example, to find the specific gravity of oxygen, Buff weighed a retort filled with potassium chlorate, generated oxygen from this, measured the volume, pressure, and temperature of the gas, and weighed the retort a second time. The difference between the two weights gives the weight of the oxygen measured. Conversely, Marchand led the still unknown quantity of oxygen, whose volume, pressure and temperature he had determined by the aid of an indifferent gas (carbon dioxide), over a weighed quantity of red-hot copper, which united with the oxygen to form copper oxide, so that from the increase in weight he obtained the weight of the oxygen. It is easy to see how these methods may be applied in other cases.

When great accuracy is not required, or when only small quantities of gas are at our disposal, the scale of the experiments is considerably lessened. Very often the chemist has to determine the specific gravity of gases that at ordinary temperatures possess the solid or liquid form, *i.e.* of vapours. To this end smaller bulbs of from 200 to 500 ccm. capacity are used, into which some of the substance is introduced. By exposing the bulbs to a temperature considerably (30° to 50° at least) above the boiling-point of the substance, so that a rapid evolution of gas is brought about, we can displace all the air contained in the bulb by the vapour. When the stream of vapour ceases to issue from the drawn-out neck of the bulb, this is sealed off and the temperature and barometric pressure observed. The weight is found from the difference in weight of the bulb when empty and when filled with vapour (the upward pressure being taken into account), and the volume is obtained by weighing the bulb empty and filled with water at 4°; the difference of weight in grams is equal to the capacity in cubic centimetres. It must not be forgotten that the bulb at the temperature of observation has a somewhat larger volume, because it is expanded by the heat; the increase for glass, about ·00003 per degree is inconsiderable (Dumas).

We may often save ourselves the trouble of weighing the bulb before and after the experiment by determining the weight of the vapour in some other fashion. For instance, if the vapour density of iodine is required, we have only to wash out the bulb with a solution of potassium iodide after the experiment has been made, and to titrate the resulting solution with sodium thiosulphate in order to get a very exact determination. Such expedients, however, have been as yet almost entirely neglected.

At very high temperatures, where glass is not sufficiently resistant, porcelain bulbs are used which may be closed by means of the oxyhydrogen blowpipe. As the determination of the temperature in such circumstances is by no means easy, we may avoid it by making a parallel experiment under the same conditions with air, the weight of which is also determined, preferably by measurement rather than by direct weighing. However, if weighing be preferred, a heavy gas of known density ought to be employed instead of air, in order to reduce the relative error of weighing (Deville and Troost). Iodine vapour, hitherto used for this purpose, is not suitable, as its density at high temperatures is not constant.

In a certain sense the converse of Dumas' process constitutes the method of Gay-Lussac, in which we determine, not the quantity of vapour which occupies a given volume, but the volume which is occupied by a given quantity of vapour. The method presupposes the possibility of weighing the substance in the solid or liquid state.

In the actual performance of the experiment, such a weighed quantity is introduced into a graduated glass tube filled with mercury and standing in a mercury trough. The tube must be placed in an apparatus which allows of its being maintained at a uniform temperature which can be accurately determined. The substance assumes the vaporous state, whereby mercury is displaced, the displaced volume being read off on the divided scale. The pressure on the gas is equal to that indicated by the barometer minus the height of the column of mercury still remaining in the tube; this height must, however, be reduced to 0° by making use of the known coefficient of expansion of mercury (·000182).

A variation of this method given by Hofmann, who employs long tubes and a vapour-jacket for heating, is a great improvement on the somewhat inconvenient original process.

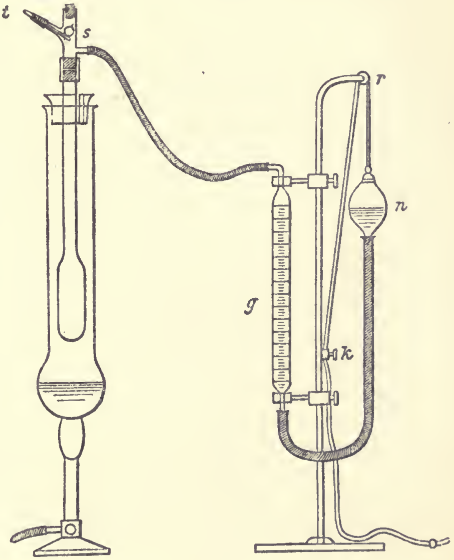

Fig. 8.

To this group also belongs Victor Meyer's method, which is likewise a very convenient one (Fig. 8). A cylindrical vessel with a long neck is heated to a suitable uniform temperature. The upper part of the vessel is put into communication with a measuring tube, and then a weighed quantity of the substance is let fall into the lower part of the apparatus. The substance in assuming the gaseous state expels an equal volume of the air which filled the vessel; this air enters the measuring tube, and from the reading the weight of the normal gas can be determined in the usual way. The method has the great advantage of being applicable at all temperatures for which resistant vessels can be made, and of a knowledge of the temperature of the vapour-chamber not being required. This temperature must, however, remain constant during the experiment.

In order to learn the temperature of the vapour-chamber, which is of importance for certain purposes, Victor Meyer drives out the contained air by means of hydrochloric acid gas and collects it over water which absorbs the hydrochloric acid. If v' is the volume of the air expelled at the temperature of the atmosphere T', and v the volume of the vapour-chamber, then the required temperature T follows from Gay-Lussac's law.

$$v' : v = T' : T$$

$$T = \frac{v}{v'}T'.$$

Other methods, to be used in special cases, have been frequently described, but they have not come into general use, and so may be neglected here.

Deviations from the Gas Law.—The first investigations on this subject were made by Despretz in 1825, though some isolated observations had already been communicated by van Marum and Oersted. He came to the conclusion that gases which are near the point where they pass into liquids are more compressible than they ought to be according to Boyle's law.

Arago and Dulong, who in 1829 took up the experiments with greater experimental means at their disposal, could discover no deviation in the case of air up to 27 atmospheres. Other gases were not investigated. Pouillet compared carbon dioxide, nitrogen monoxide, methane, and ethylene with air, and found with all these gases deviations in the same sense, namely that they were more compressible than corresponded to Boyle's law. The last two gases were not then known in the liquid state. Very comprehensive experiments were afterwards carried out by Regnault. It resulted from them that no gas was found to obey Boyle's law exactly. Besides the already known deviation of too great compressibility, hydrogen showed the opposite behaviour—was according to Regnault a "gaz plus que parfait."

However, it soon appeared that this, at first quite unexpected, behaviour is shown by all gases under very high pressures, provided they do not liquefy under the pressure. Natterer (1850) discovered this in the course of his attempts to liquefy the so-called permanent gases, oxygen, hydrogen, and air.

Interesting and inviting to further research as Natterer's results were, nearly twenty years passed before a more thorough investigation of the subject was begun. In 1870 Cailletet, and simultaneously Amagat, again took up the matter. The latter especially has greatly advanced our knowledge of the question.

The following diagrams (Figs. 9-11) give a representation of the behaviour of some gases at high pressures. The pressures are plotted on the horizontal axes; on the vertical axes we have the values of the product pv. If the gases followed Boyle's Law exactly, pv would be constant and the curve would become a straight line parallel to the horizontal axes. As we see, no gas corresponds to this simple case. Most of them exhibit a decrease of the product at low pressures, *i.e.* they are then more compressible. At high pressures, on the other hand, the product pv is without exception greater, and all the gases behave like hydrogen.

An important peculiarity shown by all gases which have been investigated at high pressures is that above a definite pressure the pv curve again becomes a straight line. The anomaly observed in the case of hydrogen at low pressures is exhibited by all gases at sufficiently high pressures. This points to the following conclusions.

The linear portion of the pv curve with variable pressure p, observable at the right side of all the curves in Figs. 9-11, indicates that there pv increases proportionally as the pressure, *i.e.* follows an equation of the form $pv = a + bp$, which may be transformed into $p(v - b) = a$.

Comparison of this equation with the ordinary gas equation, which for constant temperature has the form $pv = a$, shows that strongly compressed gases differ from gases at low pressures only in that their total volume is not inversely proportional to the pressure, but the volume becomes so after deduction of a quantity b which is independent of the pressure. That is to say, gases behave as if they consisted of an incompressible part b, and of another part $v - b$, which obeys the gas laws even at the highest pressures.

This is not inconsistent with the behaviour of gases at low pressures; the "incompressible volume" is present in this case also, but amounts to such a small fraction of the total volume, that it is negligible. For hydrogen at 0° and 76 cm. the incompressible part is only ·0006, and does not attain to 1 per cent until the pressure is 16 atmospheres. The fraction is somewhat larger in other gases, but is of the same order.

The fact that the behaviour of gases is different at moderate

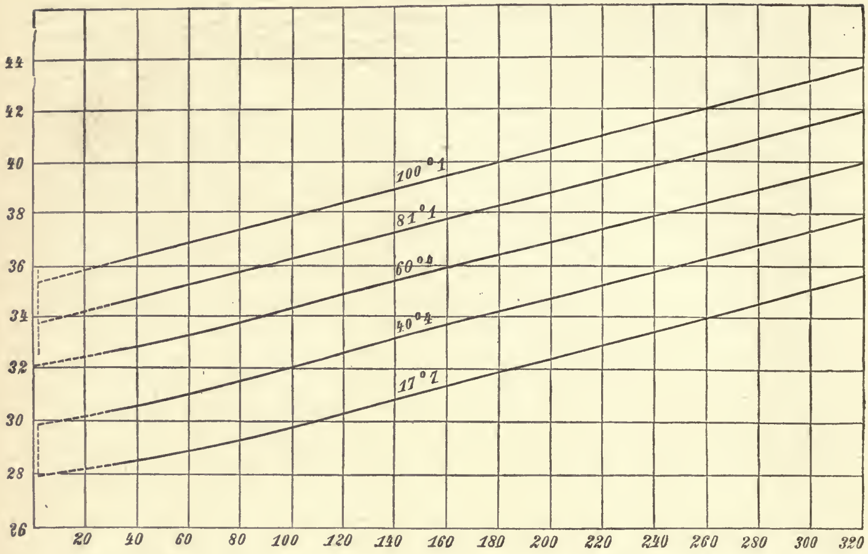

Fig. 9.—Hydrogen.

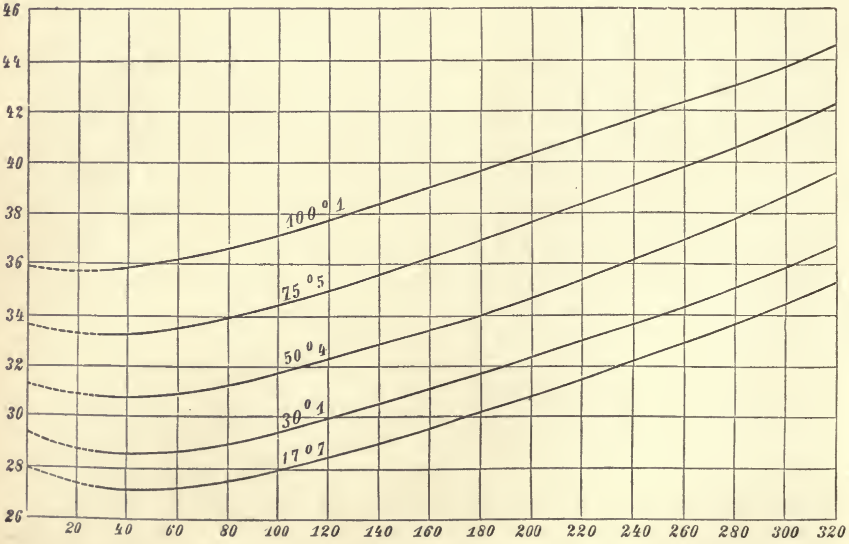

Fig. 10.—Nitrogen.

pressures and at high pressures points to the existence of some other disturbing factor. This has been found to be the density, the effects of which finally lead to the production of a liquid from the gas. This will be considered fully later.

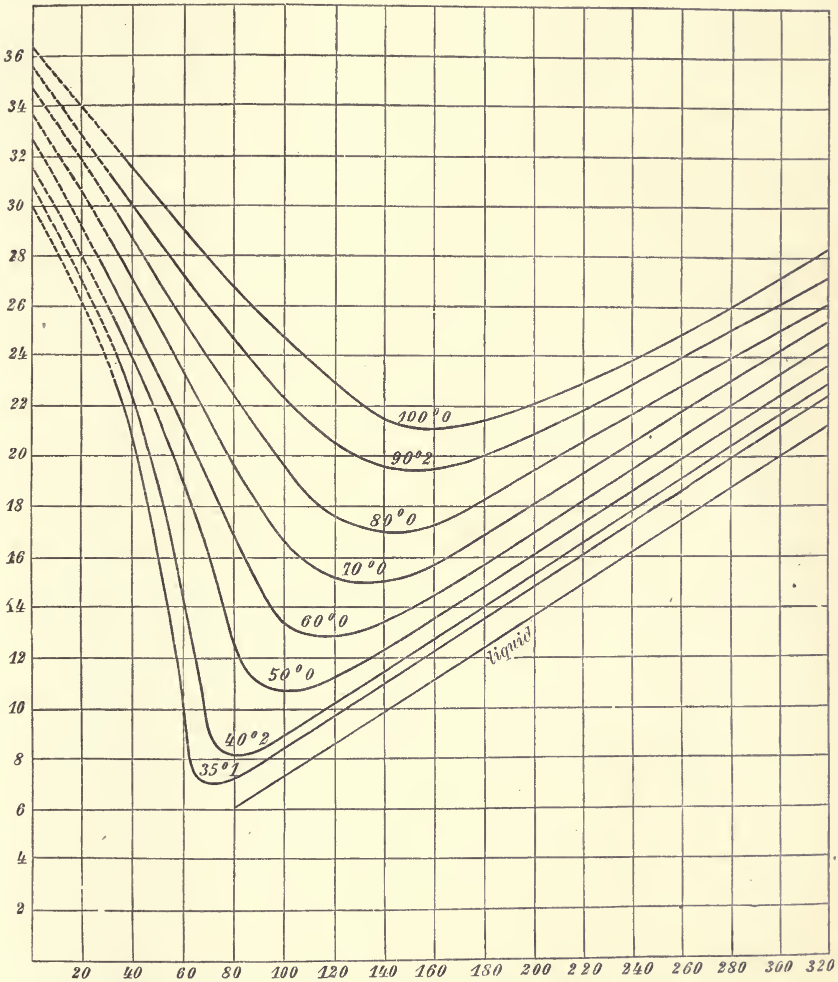

FIG. 11.—CARBON DIOXIDE.

The earlier investigations made with respect to gases at very low pressures yielded no concordant results. Recent very accurate researches by Lord Rayleigh (1901) have shown that between pressures of ·002 and ·00003 atmospheres gases follow Boyle's law exactly. If, as has been suggested from theoretical considerations, deviations again occur at exceedingly small pressures, this region seems to lie beyond the bounds of possible measurement.

The deviation of gases from the simple laws takes place not only when the pressure but also when the temperature varies. At first the coefficient of expansion as determined by Gay-Lussac as well as by Dalton was considerably too high. After the correction of the value by Rudberg, Magnus investigated several gases and found marked differences between them. As in the other case, the deviations are greatest with the most dense gases, and the coefficients of such gases are greater than those of normal gases. These deviations from Boyle's law are such that they become smaller as the temperature increases. This is easily recognised in Figs. 9-11, the curves being flatter and more horizontal the higher they lie.

The pressure increases if the gas is not allowed to expand. The pressure coefficient is also constant and equal to the coefficient of expansion only in the case of ideal gases. The deviations observed are of the same order of magnitude in the two cases. But these rules only hold for moderate pressures; at high pressures the two coefficients may be either larger or smaller than the normal. This also may be deduced from the curves of Figs. 9-11, but the mere suggestion must suffice.

As already mentioned, the divergence from the laws is greatest when the gases are near the point of condensation. The differences shown by certain gases, of which nitrogen peroxide is the best example, are of quite a different nature from those divergences which are due to the density of the gas, and lie within moderate limits at not too high pressures. They are much larger and are confined to definite moderate limits of temperature and pressure. The explanation is to be found in the variation of the gas constant r, which is connected with the change of colour and other properties of the gas. That is, they comprise gases which undergo reversible chemical changes.

But these considerations have already taken us from the general to the special properties of gases; they must therefore be deferred.

CHAPTER IV

LIQUIDS

General.—There is a very important difference between gases on the one hand and liquids and solids on the other, in that there are no specific properties of the latter states which are quantitatively the same for all substances in the same state of aggregation, such as the influence of pressure and temperature on the volume of gases. These influences vary with the nature of the substance just as do the density and the colour of gases. Even those properties which are characteristic of the liquid or of the solid state, fluidity and rigidity, are characterised by special coefficients, which are different for but are peculiar to the individual substance.

The cause of this difference of behaviour is that the density of substances in the liquid and solid states is much greater than is the case with gases. It has already been mentioned that the deviations of real gases from the ideal gas laws do not follow any general rule, but differ for different substances, and not merely to different extents according to the nature of the substance, but even in direction. We have here the influence of the constants of the substance, which in the liquid and solid states becomes predominant.

Liquids, in contrast with gases, possess a definite or specific volume. Since the volume is proportional to the quantity, and the latter is of no account in characterising the substance, the absolute volume is not a constant of the substance. The quantity is proportional to the mass, and therefore to its numerical equivalent, the relative weight; and the ratio between the volume and weight or mass is independent of the quantity of substance, but is dependent on its nature, and constitutes a specific property. The two interdependent ideas are in use, specific volume and specific weight, derived by dividing the volume by the weight and *vice versa*. The first gives the volume of the unit of weight, the specific volume; the other gives the weight of the unit of volume, the specific gravity or density. Until recently, the latter idea was in most frequent use both scientifically and in daily life, but for scientific purposes the advantage lies with the conception of specific volume. Still more generally useful is the molar volume, *i.e.* the volume of chemically comparable quantities of different substances; this will be discussed later on. Numerically, the density is the quotient of the weight of the object, measured in grams, and the volume in cubic centimetres. Since 1 ccm. of water weighs 1 g., the density is practically equal to the weight of the body divided by the weight of an equal volume of water; this indicates the usual method of determining the density of a liquid. A suitable vessel (a pycnometer) is successively filled to a given volume (up to a mark or to the stopper) with water and the liquid, and the weight in each case noted. The weights of that volume of water and the liquid are found by subtraction of the previously ascertained weight of the empty vessel, and by division of the one weight by the other the density is obtained.

Many precautions must be taken in actually performing these experiments. All objects when weighed in air suffer loss of weight, due to the buoyancy of the air. The extent is dependent on the temperature and the pressure of the air at the time; an appreciable effect is also produced by variation in the amount of water vapour, and even of carbonic anhydride in the air. In the present instance, the two experiments are performed under the same atmospheric conditions, since there is only a small interval of time between them; the buoyancy is therefore the same in the two weighings. Still the effect is not completely removed, for if the buoyancy be a and the apparent weights of water and liquid be w and f, the density is $\frac{f-a}{w-a}$; *i.e.* the effect of a is greater, the greater the difference between the density of water and of the liquid.

Further, the density of water is 1 at one temperature only, viz. + 4° C. It is smaller at all other temperatures, and the calculated density would be too high. It is most convenient to make the two weighings at the temperature at which the density of the liquid is required, and to divide the quotient of the two weights (corrected for buoyancy) by the density of water at that temperature. The subjoined table gives the density and specific volume of water at different temperatures.

[TABLE

Density and Specific Volume of Water

t(°C.)	D.	V.	t(°C.)	D.	V.
0	0·999868	1·000132	20	0·998230	1·001773
1	0·999927	1·000073	21	0·998019	1·001985
2	0·999968	1·000032	22	0·997797	1·002208
3	0·999992	1·000008	23	0·997565	1·002441
4	1·000000	1·000000	24	0·997323	1·002685
5	0·999992	1·000008	25	0·997071	1·002938
6	0·999968	1·000032	26	0·996810	1·003201
7	0·999929	1·000071	27	0·996539	1·003473
8	0·999876	1·000124	28	0·996259	1·003755
9	0·999808	1·000192	29	0·995971	1·004046
10	0·999727	1·000273	30	0·995673	1·004346
11	0·999632	1·000368	31	0·995367	1·004655
12	0·999525	1·000476	32	0·995052	1·004972
13	0·999404	1·000596	33	0·994729	1·005299
14	0·999271	1·000729	34	0·994398	1·005634
15	0·999126	1·000874	35	0·994058	1·005978
16	0·998970	1·001031	40	0·99224	1·00782
17	0·998801	1·001200	50	0·98807	1·01207
18	0·998622	1·001380	60	0·98324	1·01705
19	0·998432	1·001571	70	0·97781	1·02270
			80	0·97183	1·02899
			90	0·96534	1·03590
			100	0·95838	1·04343

Compressibility.—Liquids show none of the uniformity that we found in the case of gases under the influence of pressure. The compressibility, measured by the change of volume which unit volume experiences when subjected to unit pressure, is very small; it is *e.g.* for water, only about 48 millionths per atmosphere. For other liquids it is usually greater, and is always to a great degree dependent on the temperature.

The absolute determination of this magnitude is very inexact on account of our inability to calculate with sufficient accuracy the change of volume of the containing vessel. Relative determinations are easier to make; and if the absolute compressibility of one liquid is known, it is an easy matter to calculate others from a relative determination. For this purpose, the data for mercury are used, the compressibility of which at 0° C. is 0·0000038, *i.e.* less than 4 cubic mm. per litre for a pressure of 1 atmosphere. The difference between the apparent diminution of volume of mercury, produced by a given pressure in any given vessel, and the diminution calculated from the true compressibility, is equal to the change of volume of the vessel. Once this is known, the real diminution of volume of any other liquid is easily calculated from the apparent change in volume, and from it the compressibility or the coefficient of compression.

Thermal Expansion.—The expansion of liquids by heat is also greatly dependent on their nature, and is not yet susceptible of treatment from a general standpoint. Whilst for gases the equation holds $V_t = V_0(1 + \alpha t)$, where α is the coefficient of expansion, higher members of the series must be added to represent the influence of temperature on the volume of liquids, $V_t = V_0(1 + at + bt^2 + ct^3 \ldots)$. In other words, the temperature coefficient varies with the temperature. Such formulae have no theoretical significance, and their only use is to calculate the volumes for intermediate temperatures at which no direct observations have been made. The same service is rendered by curves, whose abscissae represent the temperatures and ordinates the volumes, or better the changes of volume.

Mendelejeff (1884) has proposed a formula which represents the expansion of liquids with considerable accuracy, although only one constant is used. It has the form $V = \frac{V_0}{1 - kt}$, and agrees tolerably well with the observed data. The variations from it, however, are mostly larger than can be explained by errors of experiment, and Mendelejeff therefore considers his formula as a law like the laws for gases, which an ideal liquid would follow exactly, but from which actual liquids diverge more or less, according to circumstances. No investigations as to the connexion between the magnitude k—the "modulus of expansion"—and the composition of liquids have as yet been undertaken.

Water occupies quite a peculiar position with regard to expansion by heat, as Rumford showed in 1802. On heating from 0° it contracts until it occupies a minimum volume at 4°, whence on further heating it expands like all other liquids, expanding the more the higher its temperature already is. Between 0° and 100° it expands some 4 per cent of its volume at 0°, one-fourth of this expansion taking place between 0° and 50°, and the remaining three-fourths between 50° and 100° (*cf.* the table on p. 53).

As different liquids behave differently towards external pressure and heat, it is to be concluded that their volume is not conditioned, like that of gases, by general circumstances which are independent of their chemical nature, but rather by their special nature.

Surface Tension.—A characteristic phenomenon of liquids, which is entirely wanting in gases, is the formation of a surface. Such a surface is always spontaneously formed when a liquid is placed in a larger space than corresponds to its own volume under the existing conditions.

The surface is generally plane, but this is because the liquid is usually under the influence of gravity. When this is excluded, a force is exerted which strives to diminish the surface as much as possible. Work is necessary to create or to increase the surface;

work can accordingly be obtained by its diminution. The surface of a liquid is thus the seat of a form of energy, which is conditioned by the existence of the surface and is changed in magnitude with a change in its extent. This is the Surface Energy; it may be regarded as characteristic of the liquid condition, just as volume energy is the most important form of energy in gases. It will be shown later that, so far as general laws are concerned, there are well-marked analogies between the two.

Vaporisation and Liquefaction.—In general a liquid can only exist under definite conditions of temperature and pressure. If the pressure is lowered by increasing the volume, or the temperature raised by external heating, a point is reached where a gas appears along with the liquid, and by further increase of volume or of temperature, the whole liquid is converted into gas. A gas formed from a liquid, or capable of being turned into a liquid in such a manner, is usually called a vapour.

These processes are reversible. If the volume of a gas is diminished, and the temperature lowered, a temperature and pressure are reached at which a liquid separates from the gas, and finally nothing is left but liquid.

These are real chemical changes, although of the simplest kind, according to the definition of chemical change as the disappearance of certain substances and the formation of others. It is sometimes said that it is better to consider vaporisation and liquefaction as physical processes. Nomenclature is always arbitrary and influenced by practical considerations, but there is this to be said, that these processes are very similar in many respects to those which are generally acknowledged to be strictly chemical processes, *i.e.* there are general laws which embrace both groups of phenomena. This is quite a sufficient practical reason for classing changes in the state of aggregation as chemical processes, more especially as a knowledge of them is of fundamental importance for all chemical work.

Every liquid can be changed into its vapour at any temperature by diminution of pressure, although at low temperatures the pressure is so small that it is barely, if at all, recognisable. But it must not be assumed that every gas can be liquefied by increase of pressure alone. There is a temperature limit, above which liquid is not produced by the greatest pressure. This is the Critical temperature, and the special behaviour at this point will be fully dealt with later.

Pure Substances and Solutions.—The laws enumerated above hold for all bodies which are uniform or homogeneous, *i.e.* in which parts with different specific properties cannot be recognised. Want of uniformity is observed in mixtures, and optical methods generally suffice for their recognition. If the parts of a mixture are of different colour, mere inspection, with or without the aid of a microscope, is sufficient. If the colour be the same, *e.g.* all white, it can be said in general that any turbid or whitish-opaque body is a mixture, while a homogeneous body is always transparent, though the transparency may be slight because of absorption of light. Thus, transparent water and glass become turbid and opaque when in a state of fine division and mixed with air. The converse is not always true, for if the particles are much smaller than the wave-lengths of light, a mixture will appear transparent.

Mixtures of gases do not exist, for whenever two gases are brought together, they unite (except when profound chemical change occurs) to a uniform gaseous system, in which, after a sufficient lapse of time, different components cannot be found by optical or other methods. Uniform systems which are formed of substances with different specific properties are known as Solutions. Gaseous solutions behave, with respect to temperature and pressure, in the same manner as the substances from which they were made, *i.e.* they obey the general gas law $pv = rT$. The gas laws, then, afford no criterion of the existence of a gas solution. For instance, atmospheric air is a gas solution (of nitrogen and oxygen), and yet the gas laws were first based on it, before their validity had been tested on pure gases.

The formation of a solution by bringing together two different liquids is not so general as it is with gases, although it may be said that a solution will always be formed if a very little of one liquid is brought together with a very large amount of another. Even then the limit is frequently reached. There are many cases in which, just as with gases, uniform solutions are formed, and these conform to the general laws of the liquids from which they are derived, *i.e.* they have definite values of density, compressibility, thermal expansion, etc.

There are, however, important differences between liquids and solutions of liquids as regards the mutual transformation of liquid and vapour. In this respect, all uniform liquids and gases are divided into two classes, pure substances and solutions. The difference is as follows.

If the temperature and pressure are changed until a liquid just begins to form vapour, it is found that the process begins at a definite temperature and pressure, which are as truly specific properties as the density, etc. With liquids of the first class, the whole liquid can be changed into vapour at this constant temperature and pressure. All that is necessary is to increase the space and to supply the heat used up in producing the vapour; if this is done, the transformation is complete without altering any other condition. The specific properties of the residue left after part has been vaporised, remain unaltered until the last drop has gone; and so, too, with the vapour. When this happens, a homogeneous liquid is a pure substance.[1]

It is characteristic of homogeneous liquids of the second class, that the formation of vapour begins at a definite temperature and pressure, but cannot be completed at them. Either the pressure must be continuously diminished or the temperature be raised, if the process is to be continued; the temperature and pressure at which the last drops vaporise are quite different from the first values. These are called Solutions.

Vapours which are formed from pure liquids behave in a corresponding manner during the change from gas to liquid. After liquid has once formed at the appropriate temperature and pressure, suitable diminution of the volume and removal of the heat set free on condensation will cause the whole of the vapour to liquefy at constant temperature and pressure; during this time the specific properties of neither liquid nor vapour suffer any change.

The vapours from liquid solutions show the solution character on liquefaction. This commences at a definite temperature and pressure, but cannot be continued under these conditions; the pressure must be continuously raised or the temperature lowered, and the last fraction of the vapour disappears at a higher pressure or a lower temperature than those at which liquid first appeared.

Uniform gases or liquids which consist of two or more gases or liquids with different specific properties always show the properties of solutions during vaporisation or liquefaction. This is the justification for applying this name to substances which cannot be vaporised or liquefied under constant conditions, although it is not known that they consist of different substances.

Since pure substances are simpler in their behaviour than solutions, we shall deal exclusively with them at present, and the consideration of solutions will be deferred. When, therefore, substances are mentioned, pure substances in the above sense are understood to be referred to.

Vapour Pressure.—From what has already been said, it follows that neither the relative nor the absolute quantities of vapour and liquid have any influence on their co-existence. According to the definition of a pure substance, any quantity of liquid can be converted into vapour, and of vapour into liquid, at constant temperature and pressure; and both can remain together unchanged so long as the volume is not altered, and no heat added or subtracted. The idea of Equilibrium may be conveniently extended to all states which do not undergo change with time, or are independent of time, in which case the relationship between vapour and liquid is an example of equilibrium. In it we have

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[1] A special case, in which constant-boiling liquids have been found to be solutions, will be explained later.

the first and simplest case of chemical equilibrium in the wider sense.

This equilibrium depends on the nature of the pure substance, and is one of its specific properties. It can occur at different temperatures, but only at correspondingly different pressures; great pressure is necessary with a high temperature for equilibrium, *i.e.* for vapour and liquid to exist together. If the pressure is fixed, the temperature at which the vapour and liquid can co-exist, which can be ascertained by starting with the liquid and steadily raising its temperature, is called the Boiling Temperature or Boiling Point; it can be recognised by the formation of bubbles of vapour. If the temperature is given, the pressure at which it is found that liquid and vapour can co-exist is known as the Vapour Pressure. Starting from gas, the Point of Liquefaction is reached, by which is meant both the temperature and the pressure at which it occurs.

It may be asked, whether there are not extreme limits of temperature and pressure, beyond which this equilibrium is no longer possible. As most liquids, it is well known, go into the solid state at low temperatures, the equilibrium between liquid and vapour must cease and give place to that between solid and vapour. The vapour-pressure at this temperature is likewise the lower limit for it. On the other side, too, there is a limit. Since the pressure rises very rapidly with increase of temperature, the density of the vapour increases rapidly and approaches that of the liquid; there is a maximun temperature and pressure at which the two densities become the same. At this point all the other properties of the liquid and vapour are the same, so that there is no difference between the two states. This is the Critical Point, and will be fully treated later; it is defined by the corresponding Critical Temperature, Critical Pressure, and Critical Volume of the substance. Below the critical temperature it is possible to convert a gas into liquid by increase of pressure alone, but not above it. Similarly, below the critical pressure liquefaction can take place on cooling, but not above it.

Liquefaction of Gases.—We should, therefore, expect any gas to be converted into liquid if it were sufficiently compressed and cooled. This expectation may be regarded as fully justified since the condensation of hydrogen by Dewar in 1898, and of helium in very recent times by Kamerlingh Onnes, who, after several attempts, obtained it in the liquid state at 4° Absolute.

The first to occupy himself in a comprehensive way with the task of liquefying the substances known as gases was Faraday (1823). He liquefied carbon dioxide, hydrogen sulphide, hydrochloric acid, sulphur dioxide, cyanogen, ammonia, and chlorine by exposing them to considerable pressure at low temperatures. Thilorier (1835) showed how carbon dioxide could be liquefied on the large scale, so that it became possible to use the liquid substance, or better the solid mixed with ether, for the production of very low temperatures, −80° to −115°. Faraday used this means in 1845 and obtained hydriodic acid, hydrobromic acid, sulphur dioxide, hydrogen sulphide, nitrous oxide, cyanogen, and ammonia, not only as liquids but as solids, while hydrochloric acid, hydrogen arsenide, ethylene, silicon fluoride, boron fluoride, and chlorine only assumed the liquid state. Hydrogen, oxygen, nitrogen, nitric oxide, carbon monoxide, and methane, on the other hand, showed no sign of liquefaction.

Afterwards, when the decisive influence of low temperature on the process of liquefaction had been made clear (see below), the method was of course indicated by which the still resisting gases might be obtained as liquids. Pictet (1877) produced very low temperatures by cooling liquid carbon dioxide by means of sulphur dioxide boiling *in vacuo*, the former in its turn being then allowed to evaporate rapidly in an exhausted space. Oxygen which was evolved in a thick-walled iron retort by heating potassium chlorate and compressed by its own pressure to several hundred atmospheres, assumed the liquid state at the temperature so obtained (−140°).

Cailletet simultaneously liquefied the "permanent" gases by using the work done by their sudden expansion for the purpose of cooling them. For different initial pressures of air there is obtained the following table, if we assume the initial temperature to be always 0°, and the final pressure 1 atmosphere.

	Temperature.	
Pressures in atmospheres.	Absolute.	Centigrade.
100	71·5	−201·5
200	58·5	−214·5
300	52·0	−221·0
400	47·9	−225·1
500	44·8	−228·2

We thus reach very low temperatures by beginning with somewhat high initial pressures. Of course those given in the table are never quite attained, for the gas, which must be in very small quantity on account of the great pressure, is at once warmed by the containing walls. Liquefaction under these circumstances is simply the production, at the instant the pressure is released, of a cloud which vanishes in a few moments.

In recent times, a continuous process has been devised by Linde and by Hampson (1895) by which atmospheric air can be liquefied in any desired quantity. The principle made use of is that air, because of its deviation from the gas laws, is cooled on expansion without doing work (*e.g.* when passed through a throttle valve). The cooling is very small, but it is used to cool down the succeeding quantities of air, when the temperature of the air passing through the valve sinks still lower. The cooling is thus increased with each passage of air through the valve, and is at length sufficient to liquefy the air. One advantage of this process is that the lower the temperature, the greater are the deviations from the gas laws, and the consequent amount of cooling on passing through the valve.

The temperature of liquid air, boiling under atmospheric pressure, varies with the percentage of oxygen, and is about $-180°$ C. By boiling it under reduced pressure we lower the temperature still more. At these temperatures almost all gases are liquid or solid, and almost all liquids pass into solid crystalline or amorphous bodies.

Degrees of Freedom.—If we compare the behaviour of a gas or liquid alone with that of the system vapour and liquid, we find a considerable difference. If a quantity of a gas be at a given temperature, its pressure is not fixed; it can assume any value by simple alteration of the volume. But if one of these is also given, the other is fixed too: any one pressure can be obtained at any one temperature only at a definite volume, and conversely. The condition of a gas is thus completely defined by two variables, or, as it may be put, a gas has two degrees of freedom. A system consisting of liquid and vapour has only one degree of freedom: if the temperature is fixed, the pressure is fixed, and *vice versa*.

The Phase Rule.—The cause of this is that such a system consists of two different parts, which are at the same temperature and pressure, but have different densities and other properties. Such different parts of a system which are physically separated from each other by a surface, are called its Phases. Within each phase the properties are constant, and each part of any phase only differs in quantity from any other part of it; the properties of the phases differ from phase to phase, even when they are capable of co-existence.

Since the requirement that a second phase should exist in contact with the original phase disposes of one degree of freedom, a system must have fewer degrees of freedom the greater the number of phases in it, one degree of freedom being lost for every new phase. A single substance has two degrees of freedom, *i.e.* pressure and temperature. In such a system, a homogeneous gas or liquid alone, there is only one phase; the sum of the phases (1) and of the degrees of freedom (2) is three. If another phase appears, as in the system vapour and liquid, one degree of freedom is lost, and one only is left; the sum of the phases and degrees of freedom still remains three.

This mode of consideration appears to be merely a formal restatement of well-known facts. This is quite correct: it is, notwithstanding, of so much use in the investigation of complex systems that it is convenient to apply it in this simple case, so that we may be familiar with its use when we reach more difficult cases. The general formulation of the law, as originally established by Willard Gibbs (1876), will then be given.

It follows from the behaviour of a vapour in contact with the liquid, *i.e.* of the saturated vapour, that neither the absolute nor the relative amounts of the two phases have any effect on the pressure. This, too, is a special case of a general law: the equilibrium between any two phases is not affected by the quantities of the phases. Much use will be made of this law in what follows.

If the quantity of a phase is very small, equilibrium is affected by the quantity, and to a very appreciable extent when a certain limit is passed. This commences when the Surface Energy begins to be an important factor. Opportunity will be taken to deal with this in the appropriate chapter.

Vapour Pressure.—Equilibrium between liquid and vapour is therefore in general represented by an equation of the form $p = f(T)$, in which $f(T)$ is for the present an unknown function of the temperature, but of which, according to the law already mentioned, it is known that it increases with increase of temperature. It is also dependent on the nature of the vapour and of the liquid, and is an expression of the properties of both.

The relation between pressure and temperature in the equilibrium of liquid and vapour can be determined in two ways. The pressure, which is produced when a given space is filled with liquid and vapour and brought to the desired temperature, may be measured; or the temperature may be found at which, under the given pressure, vapour is formed in contact with the liquid. The former is the static method; it was previously employed almost exclusively, but has been shown to be the less accurate. The second or dynamic method is generally carried out by boiling the liquid at the given pressure, *i.e.* bubbles of vapour are formed by the external application of the necessary heat; it alone is used at the present time for accurate work. The temperature corresponding to any given pressure is the boiling-point of the liquid for that pressure; the pressure which is exerted at any given temperature is the vapour pressure of the liquid at that temperature.

The name vapour tension is frequently employed instead of vapour pressure. Greater consistency is much to be desired in such matters. In this book, tension will only be applied to the effects which occur in surfaces, and give rise to capillary phenomena; its dimensions are Energy/Surface. The dimensions of pressures are Energy/Volume, and of forces, Energy/Length.

Vapour Pressure Formulae.—Two different problems regarding the connexion between vapour pressure and boiling temperature confront us. We may seek for a general law, in which f(T) is replaced by a definite expression. Or, if no such general equation can be found, it may still be possible to find a simple relation between $f_1(T)$ and $f_2(T)$, by means of which the data for one liquid can be deduced from an empirical knowledge of the other. It may be said at once that neither of these problems can be regarded as completely solved.

As to the general vapour pressure formula which would give the course of the function, it is known that over large portions of the curve it is similar to an exponential function, so that the logarithm of the pressure increases proportionally to the temperature. This is, however, only a rough approximation, since for equal differences of temperature the differences of the logarithms are not constant, but decrease slowly with increase of temperature. So far, no simple expression has been found for this decrease.

Bertrand (1887) has given an interpolation formula which is of use for purposes of calculation. It has the form

$$p = G\left(\frac{T-\lambda}{T}\right)^{50};$$

in which G and λ are constants.

The reason for the failure to bring such a general phenomenon as vaporisation under a simple formula, when the properties of gases allow of it, is that both liquid and vapour take part in the equilibrium. Simple relationships hold for vapours so long as their densities are not too great, but individual liquids (p. 51) differ in their behaviour. The properties of both phases are concerned in the vapour pressure, and so, owing to the simple behaviour of gases, there is an approximation to simple relations, which is obliterated by the individual influence of the liquid phase. For this reason, vapour pressure is a good means of gaining information regarding the effect of temperature on the properties of liquids, thus paving the way for their more general treatment.

In the absence of a general formula, more successful attempts have been made to find relations between the vapour pressures of different substances, so that if the course of the function of one liquid is known, the vapour pressure of another liquid can be deduced, when its vapour pressure has been determined at one or two points.

The first essay was made by Dalton (1801). He stated the rule that liquids having different boiling-points exhibit the same vapour pressure at temperatures removed by the same number of degrees from their boiling-points. Water boils at 100°, ether at 35°, *i.e.* they each have at these temperatures a vapour pressure of 76 cm. At 80°, 20° below the boiling-point, water has the vapour pressure 35·5 cm.; ether at the corresponding temperature of 15°, the pressure 35·4 cm. The numbers agree admirably; Dalton, in fact, deduced his "law" from the comparison of water and ether. Alcohol, on the other hand, which boils at 78°, has at 58° a pressure of 33 cm., which is considerably too low, and the same holds for most other substances.

Dühring's rule, formed after Dalton's, agrees much better with experiment. It consists in the modification of Dalton's formula by the introduction of a factor depending on the nature of the liquid. When we pass from temperatures of equal pressure to other temperatures of equal pressure, the differences of temperature are not equal, as they would be according to Dalton, but always proportional. In other words, Dalton's rule would hold if a special scale of temperature, proportional to the centigrade scale, were used for each liquid. If we take water as the liquid for comparison, Dühring's formula is

$$t' = \theta + q(t - 100).$$

100 is the boiling-point of water and θ that of the liquid at 76 cm., t and t′ the boiling-points at any other pressure, and q a factor which varies, according to the nature of the liquid, between ·5 and 2·3. To calculate q we have $q = \frac{t' - \theta}{t - 100}$, *i.e.* we merely take the ratio of the differences of the boiling-points at any two pressures.

Another formula which also gives a good approximation, especially with closely related substances, rests on the assumption that the boiling-points in degrees Absolute for the same pressures are proportional to each other. T_1/T_2 is thus a constant, if T_1 and T_2 are the boiling-points of two substances at equal pressures. Ramsay and Young (1886) have shown that this holds for the halogen derivatives of benzene, and for a large number of esters of fatty acids.

When it does not hold, it can be replaced by the more complicated equation

$$T_1'/T_2' = T_1/T_2 + c(T_1' - T_1)$$

in which T_1' and T_2' represent the boiling-points at some other pressure, which is the same for the two substances. This equation passes into the simpler one when $c = 0$.

The Critical Phenomena.—When the temperature of a vapour in equilibrium with a liquid is raised, the vapour is affected in two ways. If the pressure is kept constant it will expand owing to the increase in temperature. But the pressure will also increase and the vapour will become denser. The latter effect is by far the greater, and without exception, the density of a saturated vapour increases with rise of temperature.

Suppose the temperature to be steadily increased, the density of the vapour will steadily approach that of the liquid, and will at last reach it. With this equalisation the other properties have become equal too, *i.e.* at this point the vapour and the liquid have become identical. A liquid which up to this point occupied a given space, and was distinguishable from its vapour by the boundary surface between them, would fill the space uniformly from this point, and the interface would be no longer recognisable. This phenomenon was first observed by Cagniard-Latour (1822).

It might be supposed from this that a gas need only be subjected to sufficient pressure to be converted into a liquid. Natterer (1848), however, failed to liquefy oxygen, nitrogen, and hydrogen, even at very high pressures, although a number of other gases had been liquefied by Faraday (1823 and 1845) by means of high pressures and strong cooling.

Andrews (1869) explained this anomaly by showing that the temperature is as important a factor as the pressure in the liquefaction of gases. His observations were made on carbon dioxide and will serve here as illustrations.

If the gas at room temperature, about 18°, is subjected to increased pressure, the volume diminishes at first according to Boyle's law, but afterwards more rapidly. At 60 atmospheres liquid begins to separate, and further diminution of volume occurs without any increase of pressure until all the gas has become liquid. This is the usual behaviour of a vapour.

On repetition of this experiment at a temperature above 31°, no liquid is obtained however high the pressure. The contents of the tube in which the experiment is made remain uniform. Further investigations show that the limiting temperature is 31·4°; below 31·4° carbon dioxide can be compressed to a liquid, but not above 31·4°. This temperature may be regarded as the limit of the liquid state for this gas.

The matter is not quite so simple as this. The highest pressure required to liquefy carbon dioxide is 75 atmospheres at 31·4°. If the gas is subjected to a higher pressure, say 80 atmospheres, at a temperature above 31°, and is then cooled, the pressure being maintained until the temperature is below 31°, when it is reduced, we shall have a liquid as shown by the contents of the tube boiling and being partially converted into vapour.

It is therefore possible to start with a gas and convert it into a liquid without the coexistence of two phases.

The reverse process is also possible. Carbon dioxide below 31° is liquefied by pressure, which is then increased to over 80 atmospheres; the liquid is then warmed at that pressure. At no instant is there vaporisation, in particular not even when 31° is exceeded. If the pressure is reduced when the temperature has reached *e.g.* 40°, the contents of the tube are gaseous, diminution of pressure down to atmospheric pressure causing no appearance of boiling.

The gaseous and liquid states are therefore continuous, and the discontinuity usually observed is due to the way in which the change is generally accomplished.

These relations are rendered very clear by the diagram in Fig. 12, in which the corresponding pressures and volumes at constant temperatures are represented in a co-ordinate system; the pressures in atmospheres are plotted on the upright axis, and the volumes in arbitrary units on the horizontal axis.

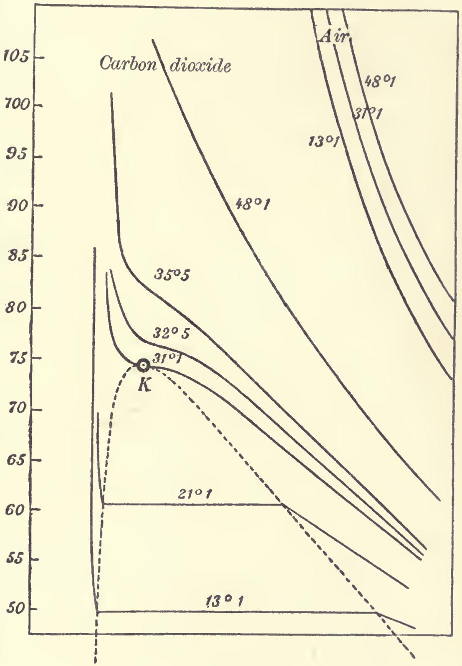

FIG. 12.

The curves for constant temperatures, or isothermals, of a perfect gas are represented in such a system by hyperbolae, corresponding to the equation pv = constant. The curves for air, which are reproduced for a number of temperatures in the top right-hand corner of the diagram, deviate very slightly from this. The last curve on the right for carbon dioxide, that for 48·1°, is similar to them; it lies below the corresponding curve for air because the product pv is smaller than for air, owing to the deviation of carbon dioxide from the gas laws. The isothermal for 35·5 lies still lower, and has a marked flexure at 85 atmospheres, *i.e.* the compressibility at high pressures is small, and at this point suddenly increases. This is still more noticeable at 32·5°, and at 31·1° it is so great that at about 75 atmospheres the curve runs horizontally for a moment. At this point of the curve the compressibility is extremely great, a small diminution of pressure causing a very large increase of volume.

The curve for 21·1° is essentially different. The curve is no longer continuous, but consists of three portions which meet at an angle. Beginning on the right with large volumes and small pressures, this part of the curve belongs to the gas. At about 60 atmospheres there is an angle, and the curve becomes a horizontal straight line. This is the point at which liquefaction commences; the pressure is then independent of the volume. When liquefaction is complete, there is a sharp turn upwards, the pressure increasing very rapidly for a very small diminution of volume.

The isothermal for 13·1° is similar, except that condensation begins at greater volume and lower pressure, and the vapour disappears at a smaller volume.

If all the breaks in the curves are connected by a line, as by the dotted line in Fig. 12, all the conditions under which the two phases, liquid and vapour, can coexist lie within this curve, and the one-phase conditions outside it. Any continuous curve which we may draw on the diagram represents a connected series of states, the volumes and pressures of which can be read off on the axes; the temperatures are given by the isothermals, which are intersected by the curve. If a curve is so drawn that it avoids the two-phase region, it represents a series of homogeneous or uniform states. But the lower right-hand corner represents gas states, and the lower left-hand corner liquid states. We can therefore obtain liquid from gas (and *vice versa*) without any discontinuity of state or the appearance of a second phase, so long as temperatures and pressures within the dotted line are avoided. This is what is meant by the continuity of the gas and liquid states.

We have at the point K the highest pressure and highest temperature at which the liquid can be recognised to exist in contact with its vapour. It is the critical point, and the corresponding temperature and pressure are the critical temperature and critical pressure. The point K further represents a volume which is the critical volume with a corresponding critical density. The volume may be referred to unit weight as usual, or better to the mol, in which case it is the critical molar volume.

The experimental determination of the critical data no longer presents any serious difficulty, other than that due to the instability of substances at the high temperatures frequently necessary. The critical temperature is the most easily determined. The liquid is sealed up in a strong glass tube which it fills to about two-thirds of its capacity, and is heated slowly until a peculiar misty appearance indicates the critical state. This appearance is more easily recognised on cooling, and sharper results are obtained by frequent repetition of the experiment.

Objection might be taken to this experiment on the ground that the exact critical temperature would not be obtained unless the volume happened to be the critical volume. From Fig. 12 it is plain that a large change of volume has a small effect on the critical point, since the isothermals are here practically parallel to the volume axis.

For the critical pressure, the liquid is enclosed in a long tube connected with a manometer and with a compresser. The upper end of the tube is heated above the critical temperature, the pressure being kept below the critical pressure; this produces an interface between the liquid and the vapour. On the pressure being increased, this interface disappears, and the pressure indicated by the manometer is the critical pressure. The method was proposed by Ostwald, and first made use of by Altschul (1892).

The critical volume is more difficult to determine. As a rule, use is made of a law discovered by Mathias (1892). If the densities of the liquid and vapour are plotted on a density temperature diagram, there are two points for each temperature; these lie nearer together the higher the temperature, and at the critical point they coincide. They lie on a parabolic curve as shown in Fig. 13. The means of the two densities at different temperatures lie on a straight line $m_1m_2m_3$. The two densities are determined for a few temperatures in order to fix the direction of the middle line. The intersection of it and the ordinate at the critical temperature gives the critical density.

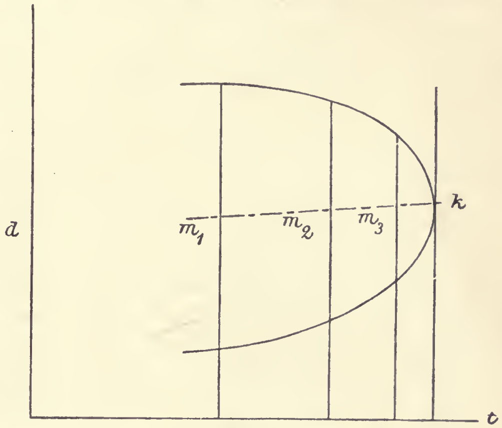

FIG. 13.

The critical constants are known for only some hundreds of substances. The critical temperatures are pretty well distributed over the whole measurable region. They are usually about half as high again as the boiling-point in absolute degrees at atmospheric pressure, but this is only an approximation.

There is much less difference among the critical pressures, which vary between 30 and 80 atmospheres. They are almost the same for closely related substances. The critical volumes are approximately proportional to the volumes at the boiling-point. These two generalisations are of some importance, and will be made use of later.

Supersaturation.—Liquefaction does not necessarily occur when a vapour is compressed to the saturation point. Vapour can persist under higher pressures than the saturation pressure and retain the properties of a gas.

The same is true for liquids. A liquid may persist at a pressure which is less than its vapour pressure at the particular temperature.

This cannot occur in the presence of the other phase; a vapour in contact with its liquid cannot be maintained at a pressure greater than the equilibrium pressure, and a liquid under a pressure below its vapour pressure is at once partially vaporised if a small bubble of vapour comes in contact with it.

The first phenomenon can be observed if the air of a large bottle containing a little water is suddenly exhausted. If the bottle has been open recently, a cloud is produced, because the temperature is lowered by the expansion of the air, and so the saturation point of the water vapour is exceeded. Condensation to liquid takes place on the dust particles, which act as "nuclei," being saturated with moisture and so acting like drops of liquid. If the bottle has stood still over night, moderate expansions produces no mist, although the cooling is the same as before; the water vapour can thus have a greater density than water vapour in equilibrium with liquid water. In this case the nuclei have either fallen to the bottom or have been deposited on the wet walls of the bottle. Condensation does occur on the walls and also at the surface of the water; but, owing to the slowness of diffusion, supersaturation persists for a long time.

The mist will appear in dust-free air too, if the degree of cooling is moderately large.

"Over-heating" illustrates the fact that a liquid may be at a pressure far below the vapour pressure without the formation of vapour. Water can be heated 100° above its boiling-point in carefully cleaned vessels, and the mercury in a well boiled-out barometer does not sink to its normal position, but remains hanging in the tube although its length may be a metre or more too high. But if the mercury has once fallen, with liberation of a very small quantity of gas, the experiment cannot be repeated until the bubbles have been expelled by boiling out again.

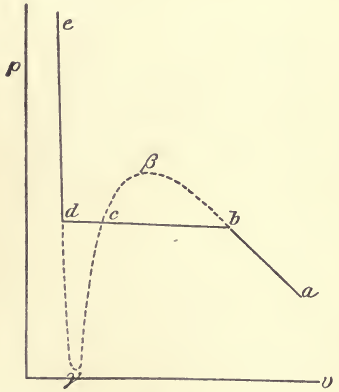

Fig. 14.

The breaks in the isothermals of Fig. 12 do not represent the end of the liquid or of the gas state, for these states can exist far beyond these points, and as has been shown experimentally, are represented by the prolongation of the isothermals.

The form of the isothermals is indicated in Fig. 14. Beginning with the gas state at a, it does not end at b, where the vapour pressure curve bd commences, but continues past b to some point β. Similarly the liquid isothermal does not end at d, the vapour pressure of the liquid, but it can be observed in the direction dγ in the region of lower pressures. This led James Thomson (1872) to suggest that the isothermals are continuous below as well as above the critical point and have the form abβcγde.

The parts bβ and dγ can be observed for some distance, but the portion βcγ is hypothetical, and, it can be predicted, will never be realised as a persistent state. While aβ and eγ represent really possible states, since the volumes diminish with rise of pressure, the change reducing the pressure, the contrary must occur in the portion βcγ. Increase of pressure would increase the volume, and the pressure would increase indefinitely, while decrease of pressure would diminish the volume, and again the change of pressure would proceed indefinitely. The states represented by βcγ, would, if realisable at all, be labile in the mechanical sense, *i.e.* they would lose their equilibrium on the slightest disturbance, and inevitably pass into some other state.

In contrast with this, ab and de represent stable states, which can return to their original condition, more or less, if they are disturbed.

The states bβ and dγ are also stable so far as changes of pressure and volume are concerned, provided that the labile region is avoided. They are, however, not stable when in contact with the other phase, but undergo finite change along the curve dcb. In view of their intermediate position these states may be termed metastable.

These phenomena are by no means confined to the change from liquid to vapour, but as a rule occur in the transformation of two phases, and the equilibrium between them. Labile, metastable, and stable states will be frequently met with later; and especially the transition from the stable to the metastable region, which is recognised by the characteristic of supersaturation, the sensibility of the system to traces of the other phase.

The Theory of van der Waals.—The theory elaborated by van der Waals (1881), as a further development of the considerations stated on p. 47, connects these and other facts in a remarkable manner. As mentioned there, in addition to the "incompressible volume," there is another factor which affects the volume in such a way that at moderate pressures the volume is smaller than it should be according to Boyle's law. Consideration of Fig. 11, p. 49, shows that this occurs to the greatest extent where the gas passes over into the liquid state. Van der Waals regards this as an effect of the mutual attraction of the smallest particles, which leads under suitable conditions to liquefaction. The facts may be expressed in this way: the internal energy of a gas is independent of the volume, if it is an ideal gas, but is not so if the gas is not ideal. The volume is not defined by the external pressure alone, but is affected by an "internal pressure" which increases as the volume diminishes. The function representing this effect has been deduced by van der Waals from considerations of a difficult and not undisputed nature. Without entering into its derivation, we may be content with the fact that the function represents the actual relations with a remarkable approach to accuracy.

Van der Waals makes the internal pressure inversely proportional to the square of the volume, so that the pressure which actually corresponds to the volume of the gas is the sum of the external pressure p and the internal pressure a/v^2. Taking into account the "incompressible volume" we have

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT.$$

If the equation is multiplied out and arranged according to powers of v, we get

$$v^3 - v^2\left(b + \frac{RT}{p}\right) + v\frac{a}{p} - \frac{ab}{p} = 0.$$

It is now of the third degree with respect to v, and has, according to the values of the constants, either three real roots, or one real and two imaginary. That is, for every value of p and T there are either one or three corresponding volumes. The first case evidently holds for the gaseous state at low pressures, and for the liquid state at high pressures, where a definite volume exists for every value of pressure and temperature. For temperatures at which the substance can exist both as vapour and as liquid there are manifestly two volumes; a third volume is not known.

If we now construct isothermals from a series of corresponding values of a and b in a co-ordinate system, we obtain curves of the same form as J. Thomson's hypothetical curve in Fig. 14. The third volume is given by the point c, and the reason of its being unknown becomes clear, for it lies in the labile region and cannot be observed.

The formula admits of a particularly satisfactory application in the case where the values of p and T are such that the three different volumes become the same. At the critical point the volume of the liquid becomes equal to that of the vapour, and as the third volume lies between them, it is therefore equal to them.

The three roots of the equation have therefore become equal. Now the value ϕ of the three equal roots of an equation of the form

$v^3 - qv^2 + rv - s = 0$ is given by $\phi = \frac{q}{3}$, $\phi^2 = \frac{r}{3}$ and $\phi^3 = s$.

We have thus $3\phi = b + \frac{RT}{p}$, $3\phi^2 = \frac{a}{p}$, and $\phi^3 = \frac{ab}{p}$, and if we denote the special values which p and T assume in this case by π and θ, we have the critical volume $\phi = 3b$,

the critical pressure $\pi = \dfrac{a}{27b^2}$,

the critical temperature $\theta = \dfrac{8}{27} \cdot \dfrac{a}{Rb}$.

These equations are very remarkable. The magnitudes a and b, which were introduced as corrections into the gas equation, can be calculated from the curves on pp. 48, 49, so as to represent the variations from the gas laws with sufficient approximation. Once they are got we can determine from them the critical constants, pressure, volume and temperature, without making a single direct experiment.

A further remarkable conclusion has been deduced by van der Waals. If in the equation

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT$$

we express the variables as fractions of their critical values, *i.e.* $p = r\pi$, $v = n\phi$, and $T = m\theta$, we have

$$\left(r + \frac{3}{n^2}\right)(3n - 1) = 8m.$$

Everything has now disappeared from the equation which depends on the nature of the particular substance, and the equation is a general relation like the ideal gas equation. The equation of state is the same for all substances if the pressure, temperature and volume are expressed as fractions of their critical constants.

When this important conclusion is put to the test, it is found to be a limiting law, similar to, but not so widely applicable as the equation for ideal gases. While the behaviour of many substances is represented with fair accuracy by the equation, the deviations cannot be ascribed to experimental error. The "Law of Corresponding States" is therefore to be regarded as a useful aid to generalisation, rather than as a strict law of nature.

There are numerous applications of this law, for we are led to expect that any peculiarity of a liquid-gaseous substance will be found to exist in other substances under corresponding conditions. For instance, all vapour pressure curves should coincide if the pressures and temperatures are expressed as fractions of the critical values. This would afford a solution of the problem on p. 62 regarding the mutual relation of the vapour pressure curves of different substances.

If the formulæ of Dühring and of Ramsay and Young are considered from this point of view, they do not satisfy the demands of van der Waals' theory. The simplest formula, according to which the temperatures of equal vapour pressures of different substances are always in the same ratio, is in closer agreement with the theory. The theory requires that equal fractions of the critical pressure should correspond to equal fractions of the critical temperature; it passes into the other equation if the substances compared have the same critical pressure. As the critical pressures in general are not far apart, the simple equation may be regarded as a proof of the approximate validity of van der Waals' equation.

Van der Waals has shown that there really is a mutual relationship between the vapour pressure curves of different substances, as required by the equation. But later measurements have demonstrated that the agreement between the theory and experiment is not exact; and this is not surprising, for the initial equation is not itself exact, but is, at best, a good second approximation.

Heat of Vaporisation.—When a liquid is converted into vapour, there is, in addition to the volume change, a thermal change, a quantity of heat disappearing, the amount of which depends on the quantity of the liquid, on its nature, and on the temperature. As the same amount of heat is liberated when the vapour is again condensed into liquid, the old theory of heat assumed that in the former process the absorbed heat was still contained in the substance, but was not recognisable by the thermometer, *i.e.* was "latent." This unwarranted assumption is no longer made. The absorption of energy is regarded as a necessary condition for the change of state, every state being characterised by the quantity of energy which is gained or lost when the substance passes into this state from any given initial state.

The heat of vaporisation is usually determined by condensing the vapour of known temperature in a vessel placed in a calorimeter, *i.e.* a vessel containing a known weight of water, and measuring the rise of temperature by means of a delicate thermometer. The product of the weight of water and the rise of temperature (after the necessary corrections have been made) gives the number of calories evolved. The quantity of heat which the condensed liquid gives up on being cooled from the temperature of liquefaction (its boiling-point at the given pressure) to that of the calorimeter must also be subtracted; this correction is found by performing a similar experiment with the heated liquid.

The heat of vaporisation is generally referred to 1 g. of substance; it is better to express them in terms of equal volumes of vapour or of the mol. The former is known as the specific heat of vaporisation, or simply as the heat of vaporisation, while the latter is the molar heat of vaporisation, and is the product of the specific heat of vaporisation and the molar weight. Molar heats of vaporisation alone are used in this book.

The heat of vaporisation decreases at higher temperatures, and becomes zero at the critical point, where the difference between the two states vanishes, and the change from one to the other is effected without any change of energy. Direct measurements of Mathias (1897) show that the values become smaller as the critical point is approached, and by a small extrapolation become zero at this point.

The general law expressing this decrease is not known; indeed, very few substances have been at all fully investigated.

The Second Law of Thermodynamics.—The properties of steam are made use of to change heat energy, produced by the combustion of coal, into mechanical energy, and this has formed the starting-point for the discovery of the general laws governing such transformations. Some preliminary explanations will make the matter more easily intelligible.

While the First Law, that of the conservation of energy, must apply to every possible transformation, it gives no indication whether or to what extent this transformation can take place in any given instance. This the Second Law does. But before this is enunciated in its most general form, we may with advantage study certain important special cases.

A quantity of heat cannot always be converted into mechanical work; it is impossible, for instance, in a space of uniform temperature, to cause the final disappearance of a given quantity of heat and the appearance of an equivalent quantity of some other form of energy in its place. Difference of temperature is necessary for such a change (Carnot, 1824), and it may be added at once that the amount transformed will be greater the greater the temperature difference is, and that at best only a fraction of the heat can be so transformed.

It can also be shown that the maximum value of this fraction, which can be transformed into some other form (*e.g.* mechanical work, which is the only one we shall consider at present), depends on the temperature only and not on the nature of the machine.

This is easily seen if we consider a machine for the transformation of heat into work, so perfectly constructed that the quantity of energy used up in friction and similar causes is negligible. The driving pressure too must barely exceed the opposing pressure. This engine would be reversible, *i.e.* if it were run in the reverse way it would use work, and the quantities of heat taken up and given out during direct driving would now be given out and taken up at the corresponding temperatures.

A further precaution must be taken in using this ideal engine. As the internal energy of the material of the engine changes with the changes of temperature and pressure, part of the heat or work might have arisen from it; it is therefore necessary to exclude this possibility by considering only processes in which the materials are brought back to their original condition, so that their energy content is the same as before. Such processes are called cycles and it must always be borne in mind that these laws only apply to reversible cyclic processes. If the laws are to be applied, the process must be represented as part of a reversible cycle.

If the engine absorbs the quantity of heat Q_1 at the temperature T_1, and converts Q of it into work, it will give up the remainder $Q_2 = Q_1 - Q$ at the lower temperature T_2. If the engine is now reversed, the amount of work Q will be used up in absorbing the heat Q_2 at the temperature T_2, and this in addition to the heat transformed from the work Q, that is $Q_2 + Q = Q_1$, will be given out at the higher temperature T_1.

Suppose another perfect or reversible engine, working between the same temperatures, but different from the first in other respects. The quantities of heat may be distinguished by a dash. The law to be proved is that $Q/Q_1 = Q'/Q'_1$, *i.e.* the ratio of the heat transformed to that taken up is the same for both, and is therefore independent of the kind of engine.

If the ratios were not the same, the engine which transforms the greater fraction of the heat in work could be run directly, and the work from it could be used to run the other in the reverse direction. The result would be that all the work delivered by the first engine would not be used in bringing the heat taken up by it, Q_1, again to the temperature T_1; an excess $Q - Q'$ would remain. This could be increased to any desired extent by repetition of the process.

If the ratio were greater in the second engine, then it would be worked directly, and the other reversely, with the same result as before.

Since, according to our assumption, the heat taken up at the higher temperature by the one engine is supplied in equal amount by the other engine, $Q_1 = Q_1'$, and $Q_2 - Q = Q_2' - Q'$. Since the work required to drive the second engine is supposed to be smaller than that supplied by the first one, Q' is $< Q$, and $Q_2' < Q_2$. In other words, any desired amount of heat will be changed into work at the lower temperature of the engines.

Now experience shows that such a transformation is an impossibility. Then the above inequalities, too, must be impossible, and the equation $Q/Q_1 = Q'/Q_1'$ must be true.

This experience is of the same general nature as the law of the Conservation of Energy, and is for this reason known as the Second Law. There are many ways of formulating it; from the present point of view it may be stated that stationary energy is not spontaneously set in motion or changed into other forms.

Perpetual Motion of the Second Kind.—The impossibility of a perpetuum mobile in the shape of an engine which turns out energy without other expenditure is a simple statement of the first law. But the idea of a perpetuum mobile, *i.e.* performance of work without expense, can be realised without necessarily breaking this law. The work which the gigantic engines of an ocean liner produces is completely changed into heat again, for even the kinetic energy of the vessel is reduced to zero at the end of the voyage, and has been transformed into heat. If the heat thus communicated to the water could be retransformed into kinetic energy, the steamer could perform its return journey without using any coal, which of course is not practicable. Speaking generally, a small fraction of the energy contained in the ocean in the form of heat would suffice to drive all the engines in the world. This would be as much a perpetuum mobile as the other, although no energy would be created out of nothing; for if the same quantity of energy could be employed again and again for the same transformation, the technical problem of the production of work without expense would be solved. This impossibility may be stated as follows: a perpetuum mobile of the second kind is impossible. By a perpetuum mobile of the second kind is meant a machine which can set stationary energy into motion or change it into other forms of energy. A perpetuum mobile of the first kind, on the other hand, would be an engine for the manufacture of energy.

The idea of stationary energy requires further elucidation, but this will be deferred until the other forms of energy are under consideration. For the present it may be said that this condition may be recognised by the fact that other states of energy pass spontaneously into this state.

The Temperature Function.—The fraction of heat transformable into work in a reversible cycle between the temperatures T_1 and T_2 is a function of the temperature alone, being independent of the nature of the engine. This accounts for the wide range of application of the second law, which is still further increased by the fact that similar laws hold for the other transformations of energy, in which heat takes no part. By the aid of this law, we can at once obtain definite relations between the quantities concerned in any transformation, and can thus arrive at a separate natural law in each case.

The temperature function which governs the transformation of heat into mechanical work, can be derived by calculating any reversible cycle of operations; we may as well choose one whose foundation is well known. Carnot's cycle (1824) of a perfect gas will serve the purpose.

We allow one mol of a gas (*e.g.* 32 g. of oxygen) to perform the following cycle, which is represented graphically in Fig. 15.

Let the gas at first have the pressure p_1 and the volume v_1 at the temperature T_1. We allow it to expand a little, the temperature remaining constant; it is necessary for this purpose that a quantity of heat Q_1 corresponding to the work should be communicated to it.

Pressure and volume are then p_2 and v_2. Next let us remove the source of heat and allow the gas to expand further. Here again it performs work, but receiving no heat from external sources, it must expend its own heat and therefore grow colder: let the temperature it reaches be T_2, the pressure and volume being p_3 and v_3. We now compress the gas. Work is required for this; let us remove the heat as it is produced so that the temperature T_2 is retained, the pressure and volume, however, becoming p_4 and v_4. Finally, let us isolate the gas and compress it further. The heat produced remains in the gas and raises its temperature, and the last part of the process is so arranged that when the gas reaches the initial temperature T_1 it shall also have the initial pressure and volume p_1 and v_1—an arrangement always possible.

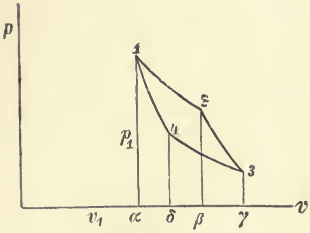

Fig. 15.

The work done by the gas in this cycle is represented by the curvilinear quadrilateral 1 2 3 4. This work, namely, is always the product of pressure and change of volume of the gas, so that the surface α 1 2 β represents the work for the passage from 1 to 2, it being always decomposable into as many small strips as we please, whose height is the pressure and whose breadth is the very small change of volume. In the same way β 2 3 γ is numerically equal to the work from 2 to 3; from 3 to 4 we have the work δ 4 3 γ; and from 4 to 1, lastly, α 1 4 δ. If the sum of the two last is subtracted from the sum of the two first, the quadrilateral 1 2 3 4 remains as the measure of the work done in the whole cycle.

Now the work which a gas can perform by expanding from the volume v_1 to the volume v_2, the temperature T_1 remaining constant, is given (p. 40), by $RT_1 \lg (v_2/v_1)$ R being the gas-constant and lg the natural logarithm. Consequently the heat Q_1 to be communicated in this part of the cycle is equal to $RT_1 \lg (v_2/v_1)$, the gas requiring no heat for mere change of volume. From 2 to 3 no heat is taken up according to our assumption. The gas on being compressed from 3 to 4, gives up a quantity of heat Q_2, specified by a similar formula, $Q_2 = RT_2 \lg (v_3/v_4)$. Between 4 and 1 again no heat enters or leaves the substance.

Consequently the ratio of the heat taken up, Q_1, to the heat given out, Q_2, is

$$\frac{Q_1}{Q_2} = \frac{T_1 \lg (v_2/v_1)}{T_2 \lg (v_3/v_4)}.$$

It can be proved that $v_1/v_2 = v_4/v_3$. For the processes 2, 3, and 4, 1, a formula developed by Poisson holds good, as heat neither enters nor leaves the system:

$$\left(\frac{v_2}{v_3}\right)^k = \frac{p_3}{p_2}, \text{ and } \left(\frac{v_1}{v_4}\right)^k = \frac{p_4}{p_1}.$$

In this equation $k = C_p/C_v$, *i.e.* to the ratio of the specific heat at constant pressure to the specific heat at constant volume. Now $pv = RT$, and in particular $p_2v_2 = RT_1$ and $p_3v_3 = RT_2$. Thus $\frac{p_3}{p_2} = \frac{v_2}{v_3} \cdot \frac{T_2}{T_1}$, and similarly $\frac{p_4}{p_1} = \frac{v_1}{v_4} \cdot \frac{T_2}{T_1}$. By substituting these values in the equations we get after a slight transformation

$$\left(\frac{v_2}{v_3}\right)^{k-1} = \frac{T_2}{T_1} \text{ and } \left(\frac{v_1}{v_4}\right)^{k-1} = \frac{T_2}{T_1},$$

i.e.

$$\frac{v_2}{v_3} = \frac{v_1}{v_4} \text{ or } \frac{v_1}{v_2} = \frac{v_4}{v_3}.$$

In this way the ratio of the two quantities of heat comes to be

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2}.$$

The amounts of heat entering and leaving the working system in this cycle are therefore in the ratio of the absolute temperatures at which they enter and leave.

By simple transformations we may bring the last equation into the following forms :—

$$\frac{Q_1 - Q_2}{Q_1} = \frac{T_1 - T_2}{T_1} \text{ and } \frac{Q_1 - Q_2}{Q_2} = \frac{T_1 - T_2}{T_2}.$$

Now $Q = Q_1 - Q_2$ is the heat transformed into work; consequently the heat transformed into work is to the total communicated heat as the difference of the temperatures between which the process takes place is to the absolute temperature of the communication; and in the same way the transformed heat is to the heat leaving the system as the difference of temperature is to the temperature at which the heat leaves.

If only small differences of temperature are considered, the work which a quantity of heat can perform in a reversible cycle is inversely proportional to the absolute temperature at which the transformation takes place.

Were it possible to reach the absolute zero of temperature, T_2 in the equation $\frac{Q_1 - Q_2}{Q_1} = \frac{T_1 - T_2}{T_1}$ would assume the value 0, and the right-hand side would become equal to unity. From this it follows that $Q_2 = 0$, *i.e.* if the lower temperature could be made the absolute zero, all the heat communicated would be transformed into work.

The quantity $\frac{Q_1 - Q_2}{Q_1}$ may be termed the economic coefficient. As the reversible cycle above described is the most perfect imaginable, it follows that the economic coefficient or the efficiency of an engine can never be greater than $\frac{T_1 - T_2}{T_1}$. A steam-engine, for example, working with steam at 150° C. and a condenser at 17° C. can at most transform only $\frac{150 - 17}{150 + 273} = \cdot 31$ or scarcely a third of the heat it receives into work. In practice the result is much less favourable.

With the same final temperature we get greater efficiency as the initial temperature rises. Between 1000° C. and 0° C. a perfect engine would transform as much as ·785 or nearly four-fifths of the heat into work.

The Vapour Pressure Formula.—The principle that the transformable heat is inversely proportional to the absolute temperature has numerous important applications.

With the help of the principle we arrive at a very important relation respecting the vaporisation of liquids. Let us consider a liquid whose volume is v_1 and which is under the pressure p_1, equal to the pressure of its vapour; let the temperature be T. If we raise the temperature by a very little, say from T to T + dT, the pressure increases by dp. Suppose the liquid to pass entirely into vapour. For this purpose we must communicate to it W units of heat, being the molar heat of vaporisation. The pressure during this time remains constant, and the volume increases very considerably; this increase, or the volume of the vapour minus that of the liquid, we shall call u. Let now the vapour be again cooled through dT, and, at the temperature T, and the corresponding pressure p, be condensed to liquid until it returns finally to its initial state. The graphic representation of this cycle is given in Fig. 16, where the work obtained is represented by the quadrilateral 1 2 3 4.

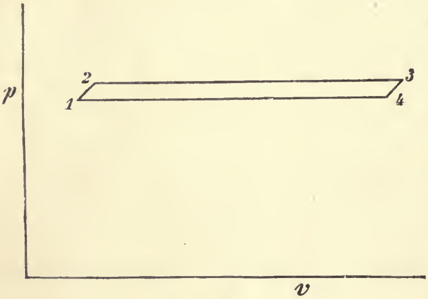

Fig. 16.

The equation
$$\frac{Q_1 - Q_2}{Q_1} = \frac{T_1 - T_2}{T_1}$$
holds good, and $Q_1 - Q_2$ being the heat transformed is equal to the

work represented by the quadrilateral 1 2 3 4. The area of this is equal to the product of the line 1 4, representing the difference of volume u on vaporisation, into the height, which is the increase of pressure dp; consequently $Q_1 - Q_2 = udp$. The communicated heat Q is the latent heat w of the vapour. For $T_1 - T_2$ we substitute dT the difference of temperature of the two operations of the cycle, and therefore obtain

$$\frac{udp}{W} = \frac{dT}{T}.$$

The equation is usually written in the form

$$W = Tu\frac{dp}{dT}$$

or

$$\frac{dp}{dT} = \frac{W}{Tu};$$

its meaning is as follows.

If the temperature is changed by the small amount dT, the vapour pressure p is changed by the amount dp. If dd in Fig. 17 represents the vapour pressure curve, a certain increase of temperature dT = ab is accompanied by a corresponding increase of pressure dp = fe. This ratio fe/cf = dp/dT is, according to the equation, directly proportional to the heat of vaporisation, and inversely proportional to the volume of the vapour; the third value can be calculated if any two of them are known. Thus there is no need to determine the heat of vaporisation if the vapour pressure curve and the density of the saturated vapour are known.

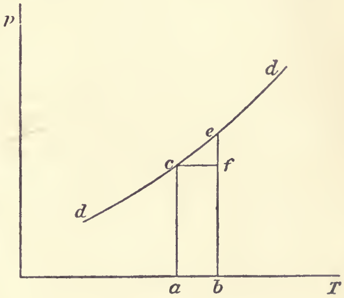

FIG. 17.

The equation assumes a very useful form of the gas laws can be held to apply to the vapour. If the volume of one mol of the vapour is substituted for u, we have u = RT/p and

$$dp/dT = pW/RT^2.$$

In this form the equation has been extensively applied, and is valid for many other relations than the simple case of the vapour pressure of a liquid. Higher mathematics show that this equation is the same as the following:

$$dlgp/dT = W/RT^2.$$

By way of illustration we may calculate by means of it the heat of vaporisation of water at 20° C, at which temperature the gas laws apply to water vapour with sufficient accuracy. In $W = RT^2dp/pdT$, $R = 8{\cdot}41 \times 10^7$, $T = 273 + 20$. The vapour pressure[1] of water is 16·319 cm. mercury at 19°, 17·363 cm. at 20°, and 18·466 cm. at 21°; $dp = 2{\cdot}147$ between the temperatures 19° and 21°, $dT = 2$, and $p = 17{\cdot}363$ is to be taken for the mean temperature 20°. The equation is

$$W = 8{\cdot}41 \times 10^7 \times 293^2 \times 2{\cdot}147/17{\cdot}363 \times 2 = 44{\cdot}7 \times 10^{10} = 44{\cdot}7 \text{ kj.}$$

Direct measurements gave 44·4 to 45·0 kj.

Although the equation enables us to calculate the heat of vaporisation from the increase of pressure with temperature, it is not possible to calculate the actual pressure from the heat of vaporisation, but only its relative increase with temperature.

The Thermodynamic Temperature Scale.—In conclusion, it may be pointed out that the equation $Q_1/Q_2 = T_1/T_2$ affords us the means of making an absolute scale of temperature, which is independent of the particular properties of any single substance. The equation was deduced on the assumption of the existence of an ideal gas, which follows the gas law $pv = RT$. By determining the extent of the deviations of a real gas from the ideal law, we can ascertain how far temperatures measured by the expansion of a gas diverge from the thermodynamically calculated temperatures. It has been found that temperatures measured by means of gases like hydrogen and helium, which diverge very little from an ideal gas, are very close to the theoretical temperatures.

Surface Tension.—The surface which liquids expose to "free" space, *i.e.* space filled with their own vapours, is of a different character from the interior owing to the effects of surface energy. Whereas every particle has freedom of motion in the interior, a particle lying at the surface can only move in the direction of the liquid; considerable forces oppose its motion out of the liquid. In the interior of the liquid every particle is equally attracted on all sides, and can therefore move as if no force acted upon it. But if it lies on the surface, the action of the adjacent particles has a resultant at right angles to the surface.

The force brought about in this fashion is very great. It can be measured in the way indicated by Stefan (1886). If we imagine a particle moving from the interior of a liquid towards the surface, half the molecular attraction must be overcome before the surface is reached, as we at once see from Fig. 18. If now the particle pursue its course further into the space above the liquid, it gets finally, altogether out of the sphere of attraction of the latter, *i.e.* becomes a particle of vapour. To bring a liquid particle into the

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[1] The pressures are not given in absolute units, because they appear in both numerator and denominator, so that the factor disappears and the formula is independent of the unit of pressure.

surface requires therefore half the work necessary to transform it into vapour. But this work is known; it is the heat of vaporisation of the liquid.

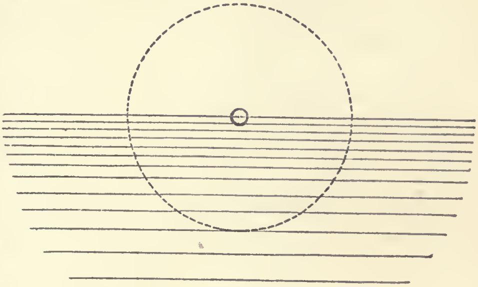

FIG. 18.

To arrive at a conception of the magnitude of the forces here in play we may make an approximate calculation. If v is the volume of 1 mol of the liquid, W its heat of vaporisation, p_2 the (unknown) surface pressure within the liquid, the "internal pressure," and p_1 the vapour pressure, the work necessary to bring the particles into the surface is $(p_2 - p_1)v$, if v may be taken as constant for a first approximation. We have consequently, according to the above,

$$(p_2 - p_1)v = \frac{1}{2}W.$$

For ether at its boiling-point, for example, $v = 107{\cdot}4$, $p_1 = 1$ atm. $W = 26{\cdot}6$ kj. $= 26{\cdot}6 \times 10^{10}$ erg; if we divide simultaneously by $1{\cdot}013 \times 10^6$ to get the pressure in atmospheres it follows, since $p_1 = 1$, that the surface pressure $p_2 = 1284$ atm.

As we see, we have here to do with very large pressures in the interior of the liquid. Of course they are not experienced by immersed bodies, because a liquid surface is formed on these also, the pressure being directed away from the body into the liquid.

A small fraction of such pressures acts in the surface of the liquid. For, if the surface of the liquid be increased, we must bring a certain number of internal particles into the superficial layer, and so perform work. Conversely, there will always be in a liquid the tendency for as many molecules as possible to pass into the interior of the liquid consequent on the molecular attraction, whereby the surface is lessened. The surfaces of liquids behave, therefore, as if under the action of a contractile force within them, which strives to reduce them to the smallest possible area.

This conception of the phenomena, deduced from the forces just considered as consequences of a surface tension of liquids, is due to Young (1804), and has proved extremely serviceable. We can, without having to overcome any other than mathematical difficulties, deduce theoretically all the corresponding phenomena, usually called capillary, from the principle that liquids strive to form the smallest surface compatible with the given conditions. The difficulties of calculation are, however, even in apparently simple cases, of more than ordinary magnitude.

In considering these phenomena, we must remember that work, *i.e.* energy, must be applied in the formation of a given extent of surface. The amount is proportional to the area, and the surface tension is got by dividing the work by the area.

To convey some idea of the numerical value of surface tension, it may be stated that the value for water at 0°, which is one of the largest known, is 77 in absolute units, or 77 ergs are used up in developing 1 sq.cm. of water surface.

Methods of Measurement.—To measure the surface tension we almost always make use of solid walls which are wetted by the liquid, *i.e.* walls on which a layer of the liquid will spread. If (Fig. 19) such a wall be dipped perpendicularly into the liquid, the whole surface abc will strive to become less and will assume the form aβc. A state of equilibrium will be reached when the weight P of the liquid raised along the wall is equal to the product of the surface tension c and the length of the line of contract l. From $P = cl$ we get $c = P/l$, or in absolute units, if g is the force of gravity acting on 1 g. (about 980 dynes):

$$cg = \gamma = Pg/l.$$

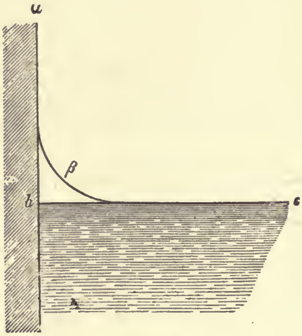

FIG. 19.

If the wall has a cylindrical form, *i.e.* if we have to do with a tube, l is in this case equal to $2\pi r$ if the circular section has the radius r, and the elevating force will be $2\pi r\gamma$. The weight raised is, on the other hand, $Pg = \pi r^2 hsg$, h being the height, πr^2 the section ($\pi r^2 h$ consequently the volume), and s the specific gravity of the column of liquid. It follows that $2\pi r\gamma = \pi r^2 hsg$ or $\gamma = \frac{1}{2}hrsg$ and $h = \frac{2\gamma}{rsg}$. The capillary height is therefore inversely proportional to the diameter of the tube, and the surface-tension is equal to half the product of the height, the radius of the tube, the specific gravity of the liquid, and the constant of gravity.

Another method of measuring surface tension consists in determining the weight of the drops of liquid supported by a given circumference. If P is the weight of the largest drop that can hang from a horizontal plane surface of circular form, and having the radius r, then $P = 2\pi r\gamma$ and $\gamma = \frac{P}{2\pi r}$. The difficulty of the method lies in the drop not separating as a whole from the surface when it falls off, but always leaving a more or less considerable portion behind.

Another method, in principle the same, is to bring a disc of known size into contact with the liquid and then determine the weight necessary just to separate the disc from the liquid. Here again we have the equation $P = 2\pi r\gamma$, where $2\pi r$ is the circumference of the disc, supposed circular.

It is assumed in all these calculations that the solid can be to this extent considered a part of the liquid, that it is in the neighbourhood of the line of contact completely overspread with the liquid, the latter meeting it with continuous curvature. It was first shown by Gauss that the liquid could also meet the solid at a finite angle α. The force then exercised by the surface tension is smaller and, as a simple geometrical consideration shows, equal to $\gamma \cos \alpha$, where α is the angle between the normal to the solid and that to the last particle of liquid at the line of contact. If the liquid wets the solid wall this angle seems always to vanish, but measurements of its exact size are difficult to make.

The Temperature Effect.—The surface tension γ depends on the nature and on the temperature of the liquid. It is very nearly proportional to the temperature, so that in general the surface tension γ at the temperature t can be given by an expression of the form $\gamma = \gamma_0(1 - at)$ According to this equation there must be a temperature at which $\gamma_t = 0$. Frankenheim (1841) pointed out that this temperature probably coincided with the critical point, (p. 64); for at the critical temperature, when liquid and vapour become identical, there can be no surface tension between them. It has been found that the critical temperature can be calculated with considerable accuracy, if the surface tension is determined at two different temperatures, and by linear extrapolation the temperature found at which the surface tension becomes zero.

The Thickness of the Surface Layer.—Further consideration of surface tension leads to the following conclusion regarding the general theory of liquids. The work required for the production of 1 sq. cm. of surface on water is 77 erg (p. 82). Now a definite quantity of water will not give an unlimited area of surface, or an unlimited quantity of energy would be associated with a finite quantity of matter which is not possible. The maximum quantity of energy which can be imparted to the liquid as surface energy is, according to the views expressed on p. 81, half the heat of vaporisation. For 1 g. of water this amounts to 2·5 kj. or $2{\cdot}5 \times 10^{10}$ erg. Then 1 g. of water will cover at most 16×10^7 sq.cm. of surface and the thickness of the layer will be $0{\cdot}6 \times 10^{-8}$ cm.

A further conclusion to be drawn from this is that the properties of substances are not the same when the dimensions of the particles fall below about 10^{-8} cm.

Negative Surface Tension.—Finally, the question may be discussed whether the tacit assumption that surface tension always tends to diminish the surface, is justified, or if there are not surface tensions which have the contrary effect and cause the surface to increase. Such tensions are known, and occur in the case of mutually soluble liquids.

At low temperatures there is a surface tension of the ordinary kind between two immiscible liquids; such as phenol and water; at higher temperatures this tension becomes smaller (while at the same time the mutual solubility of the liquids increases) and at last becomes zero. At this point the two liquids are miscible in all proportions. Liquids which are soluble in each other in all proportions may thus be supposed to have a negative surface tension. When two such liquids are brought together, the common surface strives to attain the maximum value, and this occurs when the two liquids have completely mixed. Here we have a connexion between the phenomena of solution and of surface tension.

The Vapour Pressures of Curved Surfaces.—Surface tension has an effect on the vapour pressure of liquids, though, on account of the smallness of surface energy, it only comes into play if the relative surface is very large, as in small drops. The vapour pressure of a convex surface is increased, so that the vapour pressure of a liquid at constant temperature is greater the smaller the drop is. The converse holds for concave surfaces.

The existence of this effect can easily be proved; for the total surface of two spheres is greater than the surface of one sphere which contains the same amount of substance, and therefore has the same volume. Now surface tension tends to diminish the total surface to a minimum, and therefore tends to cause two neighbouring drops to unite to form one drop. Consideration of the relative changes in surface brought about by transferring liquid from one drop to the other shows us that a large drop will increase at the expense of a smaller one; as the drops may be changed in size by a process of distillation, distillation from the smaller to the larger drops must occur in such a case. The vapour pressure of drops must therefore vary with the size of the drop.

These differences can easily be demonstrated experimentally if a (not too) volatile liquid is enclosed in an evacuated tube, and a group of drops is produced on the dry wall. After a time it will be noticed that the drops which happened to be larger than the others, are surrounded by a dry patch, the adjacent smaller drops having distilled over to their larger neighbours. Sulphur is a very suitable substance for this experiment, as it usually separates from the vapour in liquid form.

In order to calculate the difference of vapour pressure, we may imagine a capillary tube placed in a vessel containing the liquid. The liquid will rise to a height $h = 2\gamma/rs$ (p. 82). Since the system is in equilibrium, the vapour pressure at the meniscus at the upper surface of the liquid will be equal to the vapour pressure at the lower plane surface less the hydrostatic pressure of the column of vapour between the two surfaces. The latter is equal to the product of the (absolute) density of the vapour, D, and of the height h. The diminution of the vapour pressure at the meniscus dp is thus equal to Dh, or, substituting the above value of h, $dp = 2D\gamma/rs$. It is proportional to the surface tension γ, and to the ratio D/d of the densities of the vapour and liquid; and inversely proportional to the radius of the tube, or to the radius of the limiting spherical surface.

The surface in this case is concave, and causes a diminution of the vapour pressure. The surfaces of drops are convex, and the vapour pressure is increased. The corresponding experiment would be to have a liquid which does not wet the walls in a tube with a short narrow limb and a tall wide one.

Internal Friction or Viscosity.—We have hitherto treated liquids as bodies that assume any form. This is, in fact, the case, but a certain amount of work is required to effect a change in their form, and this is measured by their internal friction. It is, to be sure, in general very small, still the values are within the range of easy measurement; no ideal liquids without viscosity are known, even gases have a very small but definite viscosity. But there exist some liquids with large values for the internal friction. The greater these values become, the more do the liquids approach the solid state, and there is a continuous passage from substances like warm ether, which is excessively mobile, to those like cobbler's wax and glass, which behave in most respects like solids.

Internal friction occurs whenever a liquid moves so as to change its form, *i.e.* when the particles of the liquid change their relative positions. The coefficient of internal friction η is equal to the work required to move two surfaces 1 sq.cm. in size parallel to one another so far in one second as their distance from each other amounts to. For ordinary liquids the value of η is very small, *e.g.* for water at medium temperatures it is not more than ·011 (c. g. s.) in absolute units.

The internal friction of liquids is best determined by allowing them to run out of cylindrical tubes. For this case we have the formula $\eta = \frac{p\pi r^4}{8lv}$, where p is the pressure, r the radius of the tube, l its length, and v the volume of the liquid that flows out in unit time; π is the number 3·1416. . . . Higher mathematics is required to obtain this formula, so that here we simply state it.

The relations contained in the formula $\eta = \frac{p\pi r^4}{8lv}$, that the effluent volume of liquid is proportional to the pressure and to the fourth power of the radius, were found empirically by Hagen (1839) and Poiseuille (1843). This harmony of theory and practice confirms the assumptions made in developing the former; namely, that the internal friction is proportional to the size of the moving surface, and to its relative speed.

The formula given above is, strictly speaking, only applicable to the case in which all the work done by the pressure serves to overcome the friction. This never actually happens, as the liquid always leaves the tube with a finite velocity, consequently with some kinetic energy. If R is the part of the work used up by friction, it, plus the kinetic energy with which the liquid leaves the tube, must be equal to the total work. For the volume V of the liquid entering the tube at a pressure P, the work has the value PV, and therefore $PV = R + L$, L being the kinetic energy. This now is equal to half the product of the mass Vs (s = specific gravity) and the square of the velocity, which is equal to $\frac{V}{tq}$, where t is the time and q the cross section. We therefore get

$$PV = R + \frac{V^3 s}{2t^2q^2},$$

and

$$R = PV\left(1 - \frac{V^2 s}{2Pt^2q^2}\right).$$

A correction must still be applied to the numerical factor of this formula. It was calculated on the assumption that all parts of the flowing liquid have the same velocity. But this is not correct; the flow is faster in the middle, slower at the sides. When this difference is taken into account, a process requiring higher mathematics, the result is that instead of the factor 2 in the denominator we must put $\sqrt[3]{2} = 1{\cdot}260$; the formula remains otherwise unchanged, and as R is proportional to the coefficient η, we have

$$\eta = \eta_{\text{(observed)}}\left(1 - \frac{V^2 s}{1{\cdot}26Pt^2q^2}\right).$$

The value of the coefficient of friction deduced from the dimensions of the tube must thus be diminished in proportion to the second member within the brackets. As this member is proportional to the square of the velocity, it is best to diminish the speed of outflow as much as possible by using long tubes and small pressures.

As the determination of absolute values for internal friction is very troublesome on account of the difficulty in procuring and measuring perfectly cylindrical capillaries, we usually remain satisfied with relative values by taking the internal friction of water at 0°, or at the temperature of experiment, as standard; it is generally made equal to 1 or to 100. This mode of procedure has the great advantage that the constant of the apparatus can be determined with about the same degree of accuracy as falls to the measurements themselves, whereas individual absolute measurements are affected with much larger errors. It is left to the further progress of science to ascertain with equal accuracy the absolute value of the unit chosen.

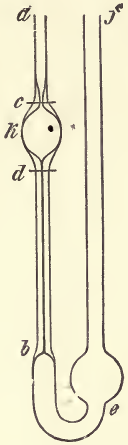

FIG. 20.

The apparatus sketched in Fig. 20 has proved to be the most convenient form for relative determinations. The essential part of the apparatus consists of a tube ab, the upper part of which is a few millimetres in width, with a constriction at c where it passes into a bulb k; below this is a capillary tube db which terminates in the wider tube be. A measured volume of liquid is introduced at f, and the time is found which the surface of the liquid takes to pass from a mark above the bulb to one below it. If t is the time for a liquid of density s, and τ that for water of density σ, the relative viscosity $\rho = st/\sigma\tau$, the pressure in the two cases being as $s : \sigma$.

CHAPTER V

SOLIDS

Energy of Form.—Mechanical energy communicated to a liquid or gas may take the form of kinetic energy or of change of volume. On restoring the system to its original volume, the energy is again given out; the only difference between the two states is that with gases this can happen at every volume, but with liquids there is at each temperature a definite volume which the liquid assumes when the external pressure is zero.

Solids are similar to liquids in respect to volume energy; they may be compressed, but at zero pressure they have a finite volume. They possess, however, another property which is characteristic of the solid state. Work is required to effect mere change of form without any change of volume, and this work is regained when the body returns to its original form.

Elasticity is the name given to this energy of form. In consequence of it, a solid retains its form so long as it is not changed by the appropriate expenditure of work, and it returns to its original form when the deforming impulse is withdrawn. A sensible degree of elasticity is the criterion of the solid state.

The property of elasticity may to some extent be masked by another property of solids. All solids have some of the properties of liquids, *i.e.* their particles can change their relative positions. Work is necessary for this, but it is not regained when the body is released from the impulse, for it has been used up by conversion into heat. This fluidity of solids is known as imperfect elasticity; it is better not to use this expression, since the property is the very opposite of elasticity. It is, in fact, a viscosity effect.

There is thus a continuous transition from the ordinary liquid state to the solid state; at least there is in the case of some substances. Molten glass at high temperatures is a liquid. On cooling, the viscosity of the glass increases; at the same time, the property of elasticity, which is hardly recognisable in ordinary liquids, makes its appearance more and more, and finally becomes the predominating character. But glass still retains at ordinary temperature some trace of liquid properties, as is shown by the well-known fact that glass tubes placed horizontally and supported only at the ends, gradually sag under the influence of gravity, and become bent. Newly made thermometers, the bulbs of which are evacuated, show the same property; and in consequence the zero point slowly rises, the mercury bulb slowly contracting under the influence of the pressure of the atmosphere.

Crystals.—Solids can be divided into two sharply differentiated groups, the amorphous and the crystalline. Substances in each group possess elasticity, but with this difference. Amorphous substances have only one coefficient of elasticity; a circular cylinder of amorphous material is deformed to an equal extent in whatever direction the pressure may be applied, nor does it make any difference in what direction the cylinder may have been cut out of a larger piece. A crystalline solid has several coefficients of elasticity; if a circular cylinder is cut out of a crystalline solid, the deformation varies with the plane in which the pressure is applied, and the number of planes which give the same effect is limited. The cylinder also has different elasticity according to the way it has been cut out of a larger piece. Cylinders only behave in the same way when they have been cut parallel to one another; further, the number of directions, except the parallel ones, which give identical cylinders is finite.

The elasticity of amorphous solids depends only on the nature of the substance and on the temperature, whereas in crystals there are, in addition, space differences.

It is, of course, assumed that we are here dealing only with uniform substances, in which similarly placed particles have the same properties. Discontinuity of specific properties is expressly excluded.

Crystal Form.—It has already been stated that solids are often so built up that their particles are arranged according to some definite law. This regular arrangement is seen wherever direction comes into question; for example in external form, elasticity, optical properties, thermal conductivity, and the like. While these properties have equal values in all directions in amorphous bodies, such as glass, they are only equal in parallel directions in crystals, as we call such bodies with regular structure; in other directions they are in general different.

Of the properties here in question the external form was the first to be noticed and investigated. Nicolas Steno (1669) discovered the law that while in different crystals of the same substance the form and size of the faces may alter in any way, the angles between the faces remain always the same.

Another regularity among the different faces of a crystal was found by Haüy (1781), who stated it as follows:—If we imagine, and this is always possible, that the simplest forms of a crystal are built up of prismatic elements with definite angles and proportions of the edges, then we can with similar prismatic elements construct all other forms occurring on the crystal, so that the surfaces drawn through the corresponding corners of the elementary prisms represent the faces of the crystal.

Crystallography received its present form from Weiss (1809), who introduced the idea of referring the different crystalline forms to definite systems of axes. The following laws on this method of representation correspond to the two just mentioned. Firstly, every substance has a system of axes whose angles and relative lengths have definite values; and, secondly, the different faces occurring on the crystal, when moved parallel to themselves to cut one axis in a given point, cut the other axes so that the segments of any of these stand in simple rational proportions to each other.

To these two laws must be added a third,—the law of symmetry, the recognition of which is also partially due to Haüy. It was enunciated in its complete form by Hessel (1830), but remained unnoticed for many years. It first gained general recognition in recent times, after it had been rediscovered by several investigators working in different ways.

The law of symmetry is to the effect that in crystals the directions in which the properties are identical, are arranged in regular order, so that superposition can be effected in n different ways, n being a finite number.

A wheel with six spokes is, in the course of one revolution round its axle, brought into superposition with itself six times. If the two sides are of the same shape, a rotation of 180° through each diameter will also bring about superposition. In contrast with this, the right and left hands can only be superposed after reflexion in a mirror.

The problem we encounter on attempting to bring all possible kinds of crystals within the compass of the general properties just enumerated, is this: In how many essentially different ways can directions in space be symmetrically arranged?

There are in all three possible ways in which superposition can be effected: reflexion in a plane, rotation on an axis, and rotatory reflexion, *i.e.* a movement consisting in rotation round an axis followed by reflexion in a plane normal to this axis. All other conceivable combinations of rotation and reflexion can be resolved into the operations already mentioned.

The simplest kind of symmetry is reflexion. It occurs when each point of the first position is related to a point of the second position in such a way that they are situated on the same normal to a given plane, and are equi-distant from the plane. The plane is called the plane of symmetry.

Rotation implies an axis of symmetry, *i.e.* a straight line round which the system can rotate in such a manner that it comes into superposition with itself. Since, in the case of crystals, the condition must be satisfied that the number of these rotations is finite, the angle of each rotation must be a rational fraction of 360°. These fractions can only be 1/2, 1/3, 1/4, and 1/6, for the other fractions would infringe the law of rational indices. The axis of symmetry must accordingly be two-, three-, four-, or sixfold; in other words, the system will be brought into superposition two, three, four, or six times during one complete revolution round the axis.

Having seen the plane of symmetry and the axis of symmetry to be the characteristics of the first and second kinds of symmetry, one might be inclined to regard the centre of symmetry as characteristic of the third kind, rotatory reflexion. It is, however, the narrower conception of the two; hence all the relations given by a centre of symmetry can be obtained from considerations of rotatory reflexion, while the converse is not true.

Rotatory reflexion can only occur with two-, four-, or sixfold axes; in the case of threefold axes two complete revolutions are required to reach the original position, the result being identical with that of a sixfold axis.

Crystal Symmetry.—By means of these eight elements of symmetry—reflexion, two-, three-, four-, and sixfold axes of symmetry, and, two-, four-, and sixfold rotatory reflexion—the symmetry properties of all crystals can be represented. On combining these elements it is soon found that the number is not very great, because it is impossible to unite every element with every other one, some being mutually exclusive, and others leading to combinations already obtained. The total number of all possible kinds of crystals is thirty-one, or, taking into account the case in which no symmetry is present, thirty-two.

We now give a short résumé of these thirty-two classes, without formally deducing them.[1]

For the sake of clearness they are generally divided into the seven crystal systems according to Weiss's system of axes.

I. Triclinic System.—The forms are the least symmetrical of all. The system contains two classes:—1. the asymmetric class without any element of symmetry; 2. the pinacoid class with a twofold rotatory reflexion. There is, therefore, a centre of symmetry, *i.e.* each surface corresponds to an opposite parallel surface and the straight lines joining corresponding points bisect each other in one common point.

II. Monoclinic System.—3. Sphenoid class: one twofold axis of symmetry. 4. Domatic class: one plane of symmetry. 5. Prismatic class: one plane of symmetry and a twofold axis of symmetry normal to it.

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[1] Groth, *Physikalische Krystallographie*, 4 Aufl., Leipzig, 1905, W. Engelmann.

The crystals of this system show a higher degree of symmetry, since the plane and axis of symmetry give rise to rectangular formation in one direction.

III. Rhombic System.—6. Bisphenoid class: three twofold axes of symmetry perpendicular to each other. 7. Pyramidal class: one twofold axis, and parallel to it, two planes of symmetry normal to each other. 8. Bipyramidal class: three planes of symmetry normal to each other, and three twofold axes normal to each other.

The crystals of this system are characterised by three axes or directions of formation intersecting at right angles, in accordance with its symmetry elements.

IV. Tetragonal System.—9. Bisphenoid class: one fourfold rotatory reflexion. 10. Pyramidal class: one fourfold axis of symmetry. 11. Scalenohedral class: one fourfold rotatory reflexion; normal to its axis, two twofold axes of symmetry normal to each other; in the axis two planes of symmetry, which bisect the angle between the two twofold axes. 12. Trapezohedral class: one fourfold axis; and in the plane normal to it, four twofold axes. 13. Bipyramidal class: one fourfold axis, and normal to it one plane of symmetry. 14. Ditetragonal-pyramidal class: one fourfold axis, and four planes of symmetry intersecting in it. 15. Ditetragonal-bipyramidal class: same as 14, with the addition of a plane of symmetry and four twofold axes of symmetry all normal to the fourfold axis.

The crystals of this system are characterised by fourfold symmetry around a Principal axis, *i.e.* one direction distinguished from all the other directions.

V. Trigonal System.—16. Pyramidal class: one threefold axis of symmetry. 17. Rhombohedral class: one threefold axis, which is at the same time an axis of sixfold rotatory reflexion. 18. Trapezohedral class: one threefold axis of symmetry, and three twofold axes normal to it. 19. Bipyramidal class: one threefold axis, and normal to it one plane of symmetry. 20. Ditrigonal-pyramidal class: one threefold axis, in which three planes of symmetry intersect. 21. Ditrigonal-scalenohedral class: in addition to the elements of class 20, three twofold axes normal to the threefold axis. 22. Ditrigonal-bipyramidal class: in addition to the elements of class 20, one plane of symmetry and six twofold axes normal to the threefold axis.

The crystals of the trigonal system are characterised by a threefold symmetry round a principal axis.

VI. Hexagonal System.—23. Pyramidal class: one sixfold axis. 24. Trapezohedral class: one sixfold axis, and normal to it six twofold axes. 25. Bipyramidal class: one sixfold axis, and a plane of symmetry normal to it. 26. Dihexagonalpyramidal class: one sixfold axis, in which six planes of symmetry meet. 27. Dihexagonal-bipyramidal class: in addition to the elements of class 26, one plane of symmetry and six twofold axes normal to the sixfold axis.

Hexagonal crystals possess a principal axis with a sixfold symmetry round it.

VII. Cubic System.—28. Tetrahedral-pentagondodecahedral class: three equal twofold axes, normal to each other; at the same inclination to these, four threefold axes. 29. Pentagonal-ikositetrahedral class: three equal fourfold axes normal to each other, four threefold and six twofold axes which bisect the angles of the fourfold axes. 30. Diakisdodecahedral class: the elements of class 28 and three planes of symmetry normal to the twofold axes. 31. Hexakistetrahedral class: the elements of class 28 and six planes of symmetry. 32. Hexakisoctahedral class: three equal fourfold axes of symmetry normal to each other, four threefold and six twofold axes, in addition to all the planes of symmetry of classes 30 and 31.

The crystals of the cubic system have three equal axes of symmetry, normal to each other, to which the other elements are added. They represent the most regularly formed crystals; in particular, class 32 contains the highest symmetry possible under the fundamental laws of crystallography.

Space Differences of other Properties.—The development of the crystal classes according to symmetry is quite independent of the external boundaries of crystals. Since crystal form is the first and most striking property of crystals, it was for long the custom to regard it as the foundation of the system of classification. Still it is only one of the many properties of crystals in which spatial relationships are to be recognised, and a complete system must embrace all these properties.

The next question is whether the differences in properties are as diverse as the kinds of symmetry, as expressed in the 32 classes. This is not the case; the 32 classes represent the greatest possible variety of symmetry relations. Different properties are of such a nature that in themselves they contain certain elements of symmetry; when this is the case, the classes which do not contain these elements, pass into the classes resulting from the introduction of these elements. In this way the number of possible differences is diminished, and the 32 classes fall into groups, each of which embraces a number of the classes.

These groups will differ according to the kind of symmetry introduced; but properties which contain the same condition of symmetry must give the same groups. This is confirmed by general experience.

The most important group is formed by properties whose symmetry is expressed in the most general case by a triaxial ellipsoid. If, for example, a source of heat is allowed to act at a point in the interior of a crystal, which is originally of uniform temperature throughout, the points of equal temperature are on the surface of a triaxial ellipsoid. This occurs in crystals of the triclinic, monoclinic, and rhombic systems. In the first, the position of the ellipsoid has no geometrical relation to the crystal form. In monoclinic crystals the axis or plane of symmetry must coincide with that of the ellipsoid; and in the rhombic system this holds for the three axes or planes at right angles to one another. These three systems form the group of triaxial crystals.

The crystals of the trigonal, tetragonal, and hexagonal systems possess an axis of at least threefold symmetry. As this is not present in a triaxial ellipsoid, it passes into a uniaxial or rotational ellipsoid. This gives the group of uniaxial crystals, or those with a principal axis.

Crystals of the cubic system have three equal axes normal to each other. With the introduction of this condition the ellipsoid passes into a sphere, and the crystals are isotropic.

With respect to such properties crystals form three groups (or five, if account is taken of the differences between triaxial crystals); and the group to which a crystal belongs can be ascertained, in spite of its arbitrary or accidental shape, by determining the degree of symmetry of some such property.

The property which has been most fully investigated is that of the propagation of light, and the related phenomena, refraction and dispersion. They are of sufficient importance to merit a separate chapter.

This character is common to all other properties which can be regarded as propagated from point to point, as conduction of heat, electricity, sound, etc. In the same category are the changes of form and of volume produced by temperature and by uniform pressure; also efflorescence, and especially chemical changes which only partially attack the crystals.

A different grouping is obtained if the properties vary with the direction, but do not discriminate between forwards and backwards. Elasticity is of this nature; a stretched rod tries to shorten, but the force does not act exclusively from one end or the other. A centre of symmetry is thus introduced; and, on this account, only so many classes of the 32 remain as are different after this condition has been added. The number of classes remaining is eleven.[1]

Polar properties, *i.e.* those which necessarily have two opposite values, as, for instance, electric charge, can only occur at axes whose ends are different, *e.g.* which are not united with a plane of symmetry

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[1] A further condition is added in the case of elasticity, which reduces the number by two classes.

at right angles to the axis. Crystals which possess a centre of symmetry are also excluded.

What has been said will show the close connexion between the symmetry of crystals and the manner in which their different properties manifest themselves. Further development of the subject belongs to crystal physics.

Regular Structure.—The only supposition made in the above development is that crystals are symmetrical systems whose diversity is limited only by the other fundamental laws of crystallography. It is, therefore, free from any hypothesis as to the internal structure of crystals, or their building up by a regular arrangement of particles. But since the beginnings of scientific crystallography down to our own day, efforts have been made to develop representations of this kind, based upon the regularities observed.

Haüy, one of the first scientific crystallographers, based his representation on the assumption that crystals are composed of smallest particles of the same shape, and in parallel positions, like bricks in a wall. On this assumption the law of rational indices at once becomes obvious. For, if parallelopiped pieces are put together in such a way that each layer has one stone fewer in the length and breadth than the layer beneath, the sides of a pyramid are obtained. If the decrease takes place only in every second or third layer, or if the layers decrease by more than one stone at a time, other pyramids will be obtained, whose relation to the first pyramid are in accordance with the law of rational indices (which Haüy called the law of decrescence, on the strength of this consideration).

While Haüy had considered it necessary to suppose his bricks to be of such a shape that the space was completely occupied by them, this idea was rejected later as unnecessary. The problem became more general, that of arranging molecules or points of mass, without regard to shape, in a regular order, and of bringing these arrangements into agreement with the facts of crystallography.

Such ideas have been developed by Frankenheim (1832-56), Bravais (1849), Möbius (1849), Sohncke (since 1867), Barlow and Pope (1906), and have led to the desired result.

Let us imagine a system of points in space, fulfilling the condition that the arrangement round any one point is the same as round any other. If we join any of these points with a neighbouring one, the straight line formed will, when produced in both directions, pass through points distant from the original points by the length of the original line; for by our assumption a third point must lie in the same relative position to the second as the second does to the first: the straight line will thus join up an infinite range of equidistant points. If we now draw a line from the point first considered to another neighbouring point the same thing holds, and it is also true for every parallel to the first straight line drawn through a point of the second, and *vice versa.* The two systems of parallels obtained by this construction lie in the same plane, and their intersections contain all the points of the system which are in that plane. The arrangement characteristic of crystals thus leads in the first instance to two systems of co-planar equidistant parallels intersecting at a definite angle. If we add the limitation that the two determining straight lines be drawn from the point of origin to the two nearest points, it can be proved that the angle must lie between 60° and 90°.

If we now draw a third straight line to a neighbouring point not lying in the same plane as the others, what we found above applies also to this line and to all parallel lines drawn through the points in the plane. All possible points arranged according to our assumption are thus determined as the intersections of three systems of parallel equidistant planes, the angles between which are subject to the condition already stated for the angle between the parallel lines. If no further condition is added we have the case of least symmetry, the asymmetric system.

But now, if we add the restriction that there shall be one plane of symmetry, this plane must evidently be at right angles to one of the planes determined by two ranges of points, and bisect the angle between these ranges; otherwise the condition of symmetry, that the arrangement on one side of the plane should be the mirror image of the arrangement on the other, cannot be fulfilled. Again, the distances between neighbouring lines in the two systems of parallels contained by the plane of the ranges must be equal. For, if we imagine one system to be drawn till it cuts the plane of symmetry, its mirror image must appear on the other side. If now the two systems of parallels be infinitely produced, the net in the plane is fully specified. We come, therefore, to the conclusion that a plane of symmetry at right angles to another plane determines in the latter a network of points with a rhombic mesh, through a diagonal of which it passes. As regards the points without the plane, we must first of all recollect that every plane containing them, and parallel to that just considered, must have exactly the same arrangement of points as the latter. Such a second field of points may thus be obtained by moving the first parallel to itself. But the demands of the law of symmetry must be satisfied. In general a parallel movement would result in the number of points being doubled by reflexion in the plane of symmetry, but this must not be the case—the points and their images must coincide; the field must therefore be shifted so that each point moves along a line parallel to the plane of symmetry. The projections on the original field of the points external to it must consequently fall on the diagonal of the rhombs through which the planes of symmetry pass. As the fundamental form of this tridimensional system of points or "space net" we thus obtain a parallelopiped with a rhombic base, each pair of intersecting sides being equally inclined to the base. By drawing the diagonals of the base, and then joining their point of intersection with the corresponding point of the opposite face we get a system of three axes, two of which are at right angles to each other and the third inclined to both. This, as we have seen, is characteristic of the monoclinic system.

We will now assume that there exists a second plane of symmetry. This necessarily calls into existence a third, which is its mirror image in the first; again, the mirror image of the first in the second determines a fourth; each of these new planes of symmetry determines three others, and so on. Two planes of symmetry placed thus at random give rise to an infinite number of new planes, all containing the same straight line. This, however, on our original assumption is impossible, so we must look for special positions in which the number of planes of symmetry remains finite. The condition for this is that the angle be $\frac{180°}{n}$, where n is a whole number.

We shall first take n = 2; the two planes cut at right angles. For the reasons given above they must both be perpendicular to a field of points. The ranges of this field must be symmetrical with respect to both planes, which condition is fulfilled either by the points forming rhombs that have the planes of symmetry for their two diagonals, or by the ranges being at right angles to each other and parallel to the planes of symmetry. The mesh of the net formed by the field of points is thus either rhombic or rectangular. The points of the parallel nets can likewise assume two positions; they may lie simultaneously in both planes of symmetry, *i.e.* perpendicularly over the lower points, or they may lie over the points of intersection of the diagonals. In both cases this takes place above and below the plane considered, which consequently proves to be a plane of symmetry. The demonstration holds in the same way for every system of more than two planes of symmetry passing through the same straight line, so that we can state in general that two or more planes of symmetry meeting in a straight line determine another such plane at right angles to that line.

Let us now reconsider our nets. When the points in the parallel plane are vertically above the middle points of the diagonals, the points of the third plane lie above those of the first. We can, therefore, consider such a system as a combination of two interpenetrating space nets. In all cases we arrive at three mutually perpendicular axes, which are not equivalent; this is the characteristic of the rhombic system.

The second plane of symmetry may now be determined by making n = 3, the angle being in this case 60°. To the first and second there is at once added a third, also at an angle of 60°. These are all prependicular to the original field of points and equivalent to one another. The only possible distribution of points in the field is that into three systems of ranges each parallel to a plane of symmetry; the points form rhombs of 60° and 120°. The first parallel plane can either have its points vertically over the original points or over the centres of the rhombs; in the latter case the points of the third parallel plane are situated vertically above the original points. For the same reasons as before the original field is also a plane of symmetry, so that the system has four in all, three making with each other angles of 60° and containing the same straight line, and one perpendicular to this line. The axes are determined by the lines of intersection of the four planes of symmetry, so that we have the hexagonal system with three equivalent axes at 60° in one plane, and a fourth at right angles to these.

For $n = 4$ there appears a second plane of symmetry inclined at 45° to the first. These two determine other two at right angles to them; so that we have four co-axial planes, those at right angles to each other being equivalent but different from the other pair. The arrangement of the points in the field can only be quadratic, and the field itself, perpendicular to the co-axial planes, must also be a plane of symmetry. The position of the points in the parallel planes is determined by the same considerations as before. The system has five axes, of which four lie in one plane and are equivalent in pairs alternately, while the fifth is at right angles to these. As a rule, we only take account of one equivalent rectangular pair of the first four, considering the other pair as secondary. This is called the quadratic system.

If we put $n = 5$ or more, we find that such a number of planes of symmetry cannot be actually realised. It was seen above that the angle contained by the lines joining a point with the two nearest points cannot be less than 60°, while five or more planes of symmetry would entail this. We have, therefore, only one step to take in order to attain the highest degree of regularity; we must make the fifth plane of symmetry of the quadratic system equivalent to two others. We then have three equivalent principal planes of symmetry at right angles to each other, and six secondary planes in addition. We have thus the cubic system.

This development does not claim to be strict or complete, but is put forward as an illustration of the considerations involved. Sohncke has made a systematic investigation of the problem, and has found that the method described above does not exhaust all the possibilities. In addition to the simple "space nets" discussed above, others, produced by placing several congruent space nets within each other, are required for a complete solution of the problem.

On comparison of the results obtained by this method with those derived from purely geometrical considerations, it is at once seen that the latter is both simpler and more complete. Thus it is not only free from assumptions, but is more advantageous from a practical point of view.

Crystallography has thus attained a position which compares favourably with that of the fundamental chemical laws of stoichiometry.

Fusion and Solidification.—It has been stated above that the amorphous solid state forms the regular continuation of the liquid state. No sudden change takes place between them, and in particular amorphous substances have no real melting-point. This passage from one state to another is so far to be compared to that of liquids into gases at pressures above the critical pressure. The passage from the liquid to the crystalline state, on the other hand, is a sudden one; it takes place at a definite temperature, at which both states can exist together, while at other temperatures only one of the two forms is stable. This is comparable to the passage of a vapour into a liquid below the critical pressure, and indeed the similarity of the two phenomena is very far-reaching.

The cause of this similarity is that this also is an instance of equilibrium between two phases (p. 61), which, according to the law, is independent of the quantities of the phases. At each pressure there is only one temperature at which the two phases can co-exist, at any other temperature one or other disappears.

The transition from one phase to the other is always accompanied by a change of energy. As in the case of vaporisation, the empirical law holds for fusion: the change from the solid to the liquid state takes place with absorption of heat, or generally of energy. The quantity of heat absorbed, the heat of fusion, depends on the nature of the substance.

There is also a change of volume on fusion, but not only the amount but even the sign varies with different substances. The volume of most substances increases on fusion, but in a few instances the converse occurs; the best known and most important example of the latter is water, the volume of which decreases about one-tenth on fusion.

Fusion differs from vaporisation also in the very small change which pressure effects in the equilibrium temperature. It is so small that it was at first quite overlooked; it was deduced theoretically by J. Thomson (1849) and experimentally discovered independently by Bunsen (1850).

The theory is quite analogous to that developed on p. 78 for the relation of pressure, temperature, and heat of transformation on vaporisation, and the considerations stated there can be immediately applied here, solid and liquid taking the places of liquid and vapour. In the equation $dp/dT = W/Tu$, as before T denotes the absolute temperature, p the pressure, dT and dp the simultaneous change in these for a given displacement of equilibrium. But W now is the heat of fusion, and u is the change in volume on fusion.

From this it is evident at once that the effect of pressure on the melting-point must be very small, since the change in volume is very small in comparison with the very large change on vaporisation, while W is also smaller, though not to anything like the same extent. There is this further difference, the volume always increases in vaporisation, but in fusion the volume may increase or decrease. In consequence, an increase of pressure does not always raise the melting-point; it may lower it. Which of the two it does, depends only on the sign of the volume change u, since W and T, the other magnitudes on the right side of the equation, are always positive.

Accordingly, the melting-point of ice, which melts with decrease in volume, is lowered by pressure, while the other substances whose volume is increased on fusion have their melting-points raised by pressure.

A numerical test of the theory is got by substituting the corresponding values in the formula. The molar volume of water at 0° is 18·02, of ice 19·66; u is thus $= -1{\cdot}66$. The heat of fusion is 80 cal. for 1 g., *i.e.* 6·03 kj. $= 6{\cdot}03 \times 10^{10}$ erg for one mol, $T = 273$. If $dT = -1$, the pressure required to lower the melting-point of ice by 1°, $dp = 138 \times 10^6$; or dividing by $1{\cdot}013 \times 10^6$ to reduce it to atmospheres, 136 atmospheres. Conversely, the melting-point of ice is lowered 0·0074° by a pressure of one atmosphere.

The Triple Point.—If another phase is added to the two: solid-liquid, the remaining degree of freedom is lost, and the system can exist at one definite temperature and pressure only. This happens when vapour is allowed to exist in contact with ice and water.

The vapour pressure of water at 0° is 4·58 mm. of mercury. At this pressure the melting-point is not exactly 0° but +0·0074°; the corresponding rise in vapour pressure does not affect the second decimal. At this temperature and pressure alone can ice, water, and water vapour coexist.

There is at least one such triple point for every substance which can exist in the three states. It is not the only possibility, however; the coexistence of two allotropic forms along with liquid or vapour gives rise to similar triple points of the same invariability.

It may be asked whether ice and water have necessarily the same vapour pressure at this temperature. The answer is in the affirmative. If it were not so, a perpetuum mobile of the second kind could be constructed (p. 74), and as this is impossible the vapour pressures cannot be different. If the vapour pressure of ice at the temperature at which water and ice are in equilibrium were a little smaller than that of water, an engine could be driven by means of the difference in pressure, water being vaporised and ice of the same temperature being formed. This ice could then be melted at the same temperature, and the cycle repeated, with the transformation of heat into work at constant temperature. This would be a perpetuum mobile of the second kind. The converse would lead to the same result, and therefore the equality of the two vapour pressures is established.

This conclusion may be briefly expressed as follows: whatever is in equilibrium in one way must be in equilibrium in every way. If ice and water in immediate contact are in equilibrium, they must be so for every other process by which, under the same conditions, ice and water can be transformed into each other. In this special case the transformation is through the medium of the vapour state. The great importance of the second law lies in this possibility of drawing conclusions from the known relations of a system in a certain respect regarding its unknown behaviour in other respects.

Overcooling.— The further question may be asked, whether this equality is preserved at other temperatures. This question has no meaning, unless both ice and water can be had at other temperatures. It has been found experimentally that water, at any rate, can be observed at temperatures below 0° in the overcooled state. Ice has never been obtained above 0°, but its existence, according to analogy, does not appear impossible. The question then turns on the nature of this overcooled state.

Fahrenheit (1724) in the eighteenth century noticed that water, enclosed in a glass bulb, could be cooled below the freezing-point, and this has since been recognised as a general property of liquids. Every liquid can be cooled below its freezing-point if it is kept from contact with the solid phase, and can remain liquid for an indefinite time. If the temperature is successively lowered, a state is reached in which solidification occurs even in the absence of the solid phase.

This is precisely similar to the behaviour of overcooled vapours (p. 67); and can be best expressed by assuming the existence of a metastable region, in which the transformation can only take place in the presence of a "nucleus" of the new phase, while further removed from the equilibrium temperature a labile region begins, in which the transformation occurs spontaneously, *i.e.* without a nucleus. The boundary between these regions is not easily observed, for it is affected not only by small differences of pressure and temperatures, which may be missed by the measuring instruments, but by the other solid substances in contact with the liquid.

The solidification of an overcooled liquid on contact with a crystal of the same substance is an effect produced exclusively by the latter. If, for instance, we dip into fused sodium thiosulphate cooled to the ordinary temperature a glass rod covered with the same salt, crystals begin at once to develop round the rod. If these are then removed carefully from the liquid so that no crystalline particle remains behind, there is no further solidification; the liquid state is retained. An overcooled liquid therefore is not *per se* in an unstable state; this is only the case when some of the solid substance is present.

The properties of an overcooled liquid are simply a continuation of those in the ordinary liquid. There is no sudden break, showing that the overcooled state is no peculiarity in the liquid, but is merely an expression of the relation between the solid and liquid forms.

In particular, the vapour pressure of a liquid as a function of the temperature is represented by a perfectly continuous curve, with no change of any kind showing at the freezing-point. Similarly, the vapour pressure curve for the solid would be expected to be equally continuous. As the two curves have one point in common at the melting-point, the two curves must either coincide throughout, or be different curves intersecting at this point.

The former was formerly regarded as the correct view, but it was based on faulty experiments; the intersection of the curves has since been proved both theoretically and experimentally. It follows from the vapour pressure formula $dp/dT = W/Tu$. The heat of vaporisation W is the heat absorbed in changing water into vapour. If ice is vaporised at the same temperature, the process can be represented as the fusion of ice to water and the change of the latter into vapour. The heat necessary for these two changes must be the same as that for the direct transformation of ice into vapour, as otherwise energy would be created in violation of the first law of thermodynamics. At the melting-point the two vapour pressures and the temperatures are the same; the only difference is in the heats of vaporisation W, which fixes the slope of the vapour pressure curve (p. 79). Since the heat of vaporisation of ice is about one-seventh greater than that of water, dp/dT must be greater to the same extent, *i.e.* the curve for ice must be steeper than that for liquid water (Fig. 21).

We obtain the numerical value of this difference by inserting the appropriate data. The vapour pressure of ice and of water at 0° is 4·58 mm., and as the gas laws may thus be regarded as valid for the vapour, the equation $dp/dT = pW/RT^2$ may be applied. It has the same form for water and ice, W in the latter case being replaced by $W + S$, where S is the heat of fusion. Subtracting the two equations $dp/dT = pW/RT^2$ and $dp'/dT = p(W + S)/RT^2$, we have on the left side the difference of vapour pressure of water and ice at the same temperature, if T and dT are the same in both cases. Making $dT = -1$, we get the difference for one degree below zero. Then $dp - dp' = pS/RT^2$, where $p = 4{\cdot}58$ mm., $T = 273$,

$S = 6{\cdot}07 \times 10^{10}$, $R = 8{\cdot}31 \times 10^7$; hence $dp - dp' = 0{\cdot}044$ mm. This is small enough to escape the notice of even a skilled experimenter. This difference, first predicted on theoretical grounds, has been confirmed by experiment in this and in some other instances, the quantitative agreement being extremely satisfactory.

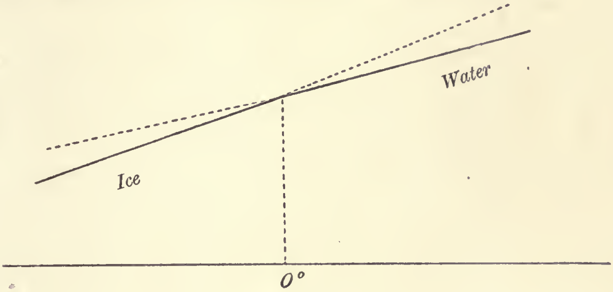

FIG. 21.

The equilibrium conditions for water in the three forms—ice, water, and vapour—can be represented on a temperature pressure diagram; we have first the vapour pressure curve of water, II; I is the vapour pressure curve of ice, intersecting the former at 0° (or more exactly, at + 0·0074°). At this point ice, water and vapour can exist together, the curve representing the effect of pressure on the melting-point, *i.e.* the ice and water curve, must therefore pass through it. Since the temperature is very little affected by pressure, the curve will be almost vertical, as indicated by III in the figure. This curve slopes a little towards the right in the case of water, which expands on solidification; for the other substances it slopes to the left. The area is divided by these curves into three fields or regions, to each of which belongs one of the three forms—solid, liquid or vapour; the curves themselves denote the corresponding pressures and temperatures at which the two adjacent phases can coexist, and their point of meeting represents the single possibility for the coexistence of all three phases.

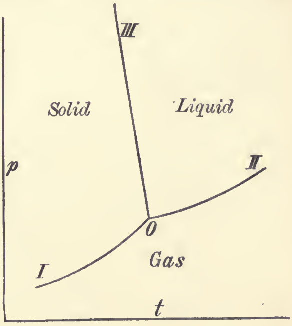

FIG. 22.

These explanations only apply to the complete stable equilibria; the metastable states extend on all sides into the adjacent regions.

Polymorphism.—The common statement that a substance can only exist in three forms—solid, liquid and gaseous—requires modification. It is generally true that only one gas and one liquid form are known, but usually there are several solid forms. That is, just as a vapour can be completely converted into a liquid with new properties, a given solid can change into another solid substance with new properties, and may under suitable conditions be reconverted into the old form. Substances are known which exist not only in two, but even in three, four or five different solid forms; no limitation to the number is known to exist. Such substances are called polymorphous. The name allotropy is commonly employed in the same connexion, especially when the substance is an element. There is no real reason for making this distinction, and it is preferable to allow the second less common name to die out.

The laws underlying the transformations of polymorphous substances are exactly the same as those relating to the change from one state to another. Accordingly it is mainly a matter of temperature. Mitscherlich, the discoverer of polymorphism, proved that of the two forms of sulphur, the rhombic is stable at temperatures below 100°, and the monoclinic at temperatures above 100°. Just as ice melts above 0°, rhombic sulphur goes into monoclinic sulphur above 100°, and returns to rhombic sulphur when the temperature is lowered under 100°, just as water freezes below 0°. Each form has a region of stability, the two regions being separated by an equilibrium temperature, at which the two forms (and the vapour) can coexist.

In a similar manner, all the other peculiarities which usually accompany the change of state are encountered, and particularly the phenomena of supersaturation which occur more readily and in both directions. Rhombic sulphur when heated above 100° does not immediately change into the monoclinic form but remains in the old state for a longer or shorter time, according to the degree of overheating. This can be carried so far that, with rapid heating, the melting-point of rhombic sulphur can be determined before it has had time to change into monoclinic sulphur. The melting-point is 115°, while that of monoclinic sulphur is 120°. It is a general rule that the less stable form has the lower melting-point.

Monoclinic sulphur is also moderately stable at low temperatures. When the transition into rhombic sulphur, which is recognised by the opacity of the crystals, does take place, it is found to start at definite points, the transition being effected by contact with the stable form. It is not quite certain whether we have here a metastable and a labile condition, as we should expect, but it is not improbable.

The difference of the vapour pressures of the solid and liquid forms of a substance at temperatures other than the melting-point also exists in this case; the vapour pressure of the stable form is always smaller than that of the less stable form at the same temperature. The two vapour pressures are the same at the transition temperature, *i.e.* at the point of intersection of the two curves.

The transformation at the transition point follows the law that the change resulting from an increase of temperature occurs with absorption of heat, as is the case in the other changes of state. It is in fact an instance of a general law that when an equilibrium point is exceeded as the result of some external influence, the process which takes place always acts in opposition to the influence, *i.e.* reduces its effect to a minimum. For instance, raising the temperature brings about reactions which are accompanied by absorption of heat, and increase of pressure is followed by the reaction which reduces the volume. Many illustrations of this law have been already given.

The transition temperature of polymorphous substances is likewise displaced by pressure. The equation for the melting-point developed on p. 102 is immediately applicable to this case. The sign of the volume change for the transformation effected by rise of temperature (*i.e.* accompanied by absorption of heat) settles whether the transition temperature is raised or lowered by an increase of pressure.

There are many other substances which exhibit the same behaviour as sulphur. But there are other polymorphous substances for which no transition point can be found; they have only one stable form, and one or more unstable forms. In these cases the transition temperature is higher than the melting-point of the less stable form, and is unattainable owing to the impossibility (p. 101) of heating solids above their melting-points. Lehmann first called attention to these two different kinds of polymorphism, designating the first as enantiotropic and the latter as monotropic.

According to the rule that the vapour pressure of a less stable form is greater than that of a more stable form, and that the vapour pressure curves of the liquid and solid forms intersect at the melting-point, Figs. 23 and 24 give the vapour pressure curves for the two cases, I referring in both diagrams to the liquid, II and III to the solid forms. The points of intersection of I with II and III are melting-points, of II with III are transition temperatures. In Fig. 23 the liquid curve intersects the other two above the transition temperature, and both solid forms have a stable region. If the intersection of I with II and III is below the transition temperature, as in Fig. 24, form II is unstable in the whole region up to its melting-point and III is stable. The first case represents enantiotropism, and the latter monotropism.

It is conceivable that the curves may intersect again at low temperatures, and the relative positions of the different forms be changed, but so far no example of this is known.

We must now consider how the unstable form of a monotropic substance can be observed, seeing that there is no region in which it is stable. It is a general rule that the unstable forms are obtained from a liquid or vapour form before the stable form appears. If no nuclei of the more stable forms are present, the first product of the spontaneous solidification of an overcooled liquid is the most unstable form. If this form is still in the metastable region, it can persist indefinitely.

The transformation of the unstable form into the stable form depends upon the presence of a nucleus of the stable form, precisely as in the case of an overcooled liquid in the metastable region; there is no difference in this respect between monotropic and enantiotropic substances.

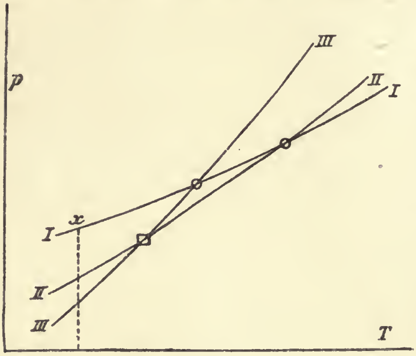

Fig. 23.

According to the above considerations, only one form of a substance can be stable under given circumstances, and this form alone should be found in nature (unless the presence of nuclei of the most stable form was excluded). This is contrary to experience; many polymorphous forms of minerals are known, in which there was ample opportunity for contact with nuclei of the other form. Calcite and aragonite, forms of calcium carbonate, are a very well-known example. Aragonite spontaneously changes into calcite at dull red heat, but the two forms can apparently remain side by side for any length of time at ordinary temperatures.

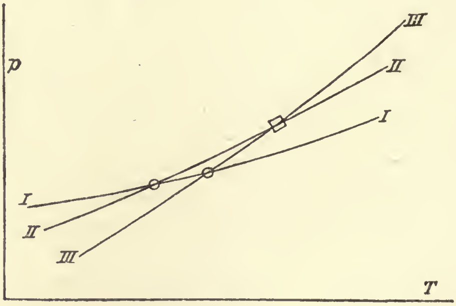

Fig. 24.

The cause of this has not been exhaustively studied. A very important factor (probably the only essential one) is the velocity of transformation, which may be very small. The velocity depends on several factors. Thus, it is smaller the nearer the temperature is to the transition temperature, and becomes infinitely small at the transition temperature. Again, the velocity may become unrecognisably small at temperatures much below the transition temperature, for all chemical processes are very much slowed down by lowering the temperature. Both circumstances may confer an apparent stability to forms which, according to the above, ought to undergo transformation. The transformation is actually going on, but at so slow a rate that it is not noticeable.

Liquid Crystals.—Increasing viscosity is, as we have already seen, an indication that there is a continuous transition between the liquid and solid states. Liquids as a rule do not possess "directional" properties, *i.e.* are amorphous; this transition, therefore, only holds for amorphous solids. But plastic deformation is not confined to amorphous substances, although it is nearly always associated with them; gold is an example of a plastic, crystalline solid. Their viscosity is usually so great that very strong forces are required to deform crystalline solids. Only in recent years have crystalline substances with comparatively small viscosity been discovered and have led to the idea of liquid crystals (Lehmann, 1889).

These substances are organic compounds; they show all gradations from the type of ordinary crystals to the most pronounced liquids. If the crystals are only soft, and not liquid, as, *e.g.* ammonium oleate, they are bounded by plane surfaces. According to the theory of surface tension the pressures at the apices and edges of crystals are very great; in consequence of which the edges are rounded off. Two crystals brought into contact flow together more or less rapidly, forming one crystal with relatively smaller surface. There is equilibrium between the directional forces of the crystalline form (which lead under suitable circumstances to plane surfaces) and the surface tension (which tends to a spherical shape), and it depends on the viscosity how soon a system, which is not yet in equilibrium, will settle down to its final condition. If the directional forces are smaller, the crystal will show only a more or less developed approximation to plane surfaces, and may become a purely spherical drop if the forces are very weak.

In the latter case the crystalline character is still shown by the anisotropic nature of the drops, which are uniaxial (p. 94). Very probably they possess other directional properties too, but nothing is known of them.

This is the explanation of their opalescent appearance, owing to which they were sometimes regarded as mixtures. As these substances have different optical properties in different directions, and as the particles are as a rule differently oriented, regions of different refractive index border on each other, and so the conditions for partial reflexion, *i.e.* opalescence, are fulfilled. Under suitable conditions they can also appear absolutely clear. This occurs when the individuals are in parallel positions.

These substances undergo the same transitions as any other of the states of aggregation. At a lower temperature they generally pass into other crystals, *i.e.* they are polymorphous; these forms differ in no respect from other crystallised substances. At a higher temperature they melt, but this is not always accompanied by any considerable fall in the viscosity (indeed there are cases where the viscosity increases), although the amorphous and ordinary liquid condition obtains. Both these temperatures are quite sharply defined, and follow the same laws as ordinary melting-points and transition temperatures. In a few cases two or more different crystalline-liquid forms have been observed, some of which are metastable and can only be obtained by overcooling.

BOOK II

STOICHIOMETRY

CHAPTER VI

EQUIVALENTS AND COMBINING WEIGHTS

Elements and Compounds.—Hitherto substances have been considered purely as substances, in so far as they are subject to general laws, *i.e.* as regards that part of their behaviour in which they differ least. But now we have the problem of examining the consequences of their mutual chemical action, and here their individual differences appear, which afford the most certain means of distinguishing one from another. In other words, we have to do with their chemical properties in the strict sense.

The principal phenomenon is that two or more substances disappear when brought together, and new substances take their place. The simplest case of appearance and disappearance has already been met with in the mutual transformations of the states of aggregation; only these took place without the formation of other substances. As a rule a pure substance remains a pure substance when it undergoes a change of state. These transformations are all reversible, so that the series of transformations runs in each direction and it is always possible to return to the initial state. It has not been emphasised that the law of the conservation of weight and mass holds for all these transformations. No circumstance is known which affects weight and mass; therefore in this particular case there is no effect.

For chemical transformations, too, in which several substances take part, the law of the conservation of weight and mass holds quite generally. It was used by Lavoisier in the last quarter of the eighteenth century to deduce that, if the weight increases during a chemical process, weighable substances must have been taken up. In this way he showed in particular that in combustions the substance has combined with a constituent of the air, since the product weighs more than the combustible did. This surplus is to be set down to the action of oxygen.

Such considerations have led to the idea of elements in the present sense. For the sake of clearness, we will confine our attention to the simplest case, where two substances are transformed into a single one, or conversely one into two; on account of the conservation of weight, the weight of each of the two is smaller than that of the single substance. The substances of smaller weight are called the components and the other the compound.

We may now inquire whether the components of one reaction may not be compounds in other reactions. If this is so, the component also has components, which are relatively simpler substances.

We may suppose this investigation to be carried out as completely as science permits, and we should have a number of substances which always appear as components and never as compounds. In other words, they always pass into substances of greater weight, and never into substances of less weight. These substances are the Elements.

According to this, elements appear to be substances of essentially the same nature as compounds. The fact that they have never been observed as compounds is no reason why they should never in the future be found to be so. Throughout the history of Chemistry it has been the case that from time to time substances, previously regarded as elements, have been proved to be compounds.

As these considerations are based upon the chemical behaviour of all substances investigated by chemists, we are justified in saying that all known substances consist of one or several of about eighty elements, *i.e.* can be decomposed into them.

The Conservation of the Elements.—The relation between a non-elementary substance or a compound and its elements is unambiguous and reversible. Unambiguous, in that only the same elements can be obtained from a given substance, no matter how the change is effected; it is reversible, because the substance can be regenerated from these elements.

The first of these rules is universally true, no exceptions being known, but the second rule cannot at present be experimentally verified in all cases. There are many substances, especially among those which occur in living organisms, of which the analysis or the testing for the elements has been made, but not the synthesis, or the building up of the substance from these elements or from simpler compounds of them. Still, the number of syntheses, even of difficult substances, is very large, and is increasing so steadily, thanks to the untiring efforts of investigators, that it is merely a question of time and work when the synthesis of any specified substance will be effected. There are no indications of the impossibility of effecting a synthesis in any given case.

These experimental relations can be most briefly expressed in the law of the conservation of the elements: it is impossible to transform one element into another element. Discoveries have been made recently, which appear to contradict this law; but it is plain that this merely involves a revision of the table of elements in accordance with the definition.

The law may be regarded as the final outcome of the efforts, which persisted through the Middle Ages, to make gold from the cheap metals, especially lead. In view of the many transformations which had been observed, it was not altogether unnatural to suppose that lead could be transformed into gold if only the right means could be found. Just as the quest after perpetual motion was practically unsuccessful, so was this; and as, in the former, the law of the conservation of energy was the positive result of these prolonged efforts, here, too, there resulted the law of the conservation of the elements. For, since gold and lead answer to the definition of elements, their mutual transformation cannot take place.

But the law predicts more than the mere exclusion of the direct transmutation of the elements. It excludes the possibility of indirect transmutation. In other words, a substance, which contains a given element A, cannot be made without using A or some substance from which A can be obtained, *i.e.* a compound of A. If this were possible, A could be made from other elements, *i.e.* the transmutation of elements could take place.

This law simplifies very considerably the relation between elementary and compound substances; the enumeration of the elements contained in any compound limits in a very definite manner the circle of substances which can possibly be prepared from it, and at the same time indicates to a greater or less extent the methods of preparation.

Acids, Bases and Salts.—Acids, bases and salts belong to the oldest groups of substances, classified according to their chemical properties. The first have a special taste, as their name indicates. As it is not always advisable to test liquids by taste, the reddening of blue vegetable colours was soon introduced as the test for acids. The bases formed a group opposed to the acids; they turn the reddened vegetable colours blue or green (the alkaline reaction), and also destroy the other chemical properties of the acids, their sour taste and corrosive action, when brought into contact and chemical reaction with them. The product formed has neither acid nor basic properties if the right proportions of the two substances have been taken; it has a salt taste and has no action on vegetable colouring matters. This is the neutral condition, and the substance is called a salt. By a suitable series of changes the same acid and base can be obtained again from the salt. For, in addition to their common properties just mentioned, these groups have other properties which enable us to recognise a large number of different acids and bases. The number of salts is larger still, for, in general, every acid can unite with every base to form a salt, and thus the number of salts formed by *a* acids and *b* bases is the product *ab*.

Constant Proportions.—In making a salt by adding a base to a given quantity of an acid, and testing the product from time to time by means of a vegetable colour (litmus), the following is observed. At first the whole remains acid, for although a part of the acid is neutralised by the base, the rest of it is unchanged. The salt has no action on the litmus, but the acid has, and the mixture has an acid reaction.

On continuing the process, a point is reached at which the acid reaction is replaced by the alkaline reaction. With greater care in adding the base, the neutral point can be obtained. Then a slight excess of base will give the alkaline reaction, or of acid the acid reaction.

There is, consequently, a perfectly definite ratio in the weight or quantity of an acid and a base which neutralise each other with the formation of a new substance, the salt. The process is a typical chemical reaction, since the original substances and their properties have disappeared and have been replaced by a new substance with its own properties, a salt. This chemical process is characterised by the definite ratio between the reacting substances.

It is not a question of absolute weights, but of the ratio of the weights. It can easily be shown that the same ratio is found whether the experiment is done on a large or on a small scale, provided that the "same" substances are used; it is also found that no other circumstance of any kind alters the ratio. The ratio of the weights in this chemical process is as unaffected by any known agency as is relative weight itself.

What has been said regarding the ratio between acids and bases in the formation of neutral salts, is true of all chemical processes, and not only when two substances change into a third, but however many substances interact and are formed. The weights of all the substances concerned are always in a definite ratio. It also holds in the case of decompositions, when from one substance two or more result, or, in general, when the number of different products is larger than the original number of substances. Only such quantities are to be measured as have really taken part in the reaction or have resulted from it.

This general law is known as the law of constant proportions. To a certain extent it has been known ever since chemical processes have been turned to industrial purposes, for it could not have escaped notice that the yield stood in a definite ratio to the amount of material taken. It was first stated as a general and strict law about the end of the eighteenth century by Proust, after C. L. Berthollet had denied its validity. In its most general form it is as follows.

If A, B, C . . . . are the weights of different pure substances necessary for the formation of P, Q, R . . . . weights of new pure substances, all these weights are in definite, unalterable ratios.

It may be remarked that this law can be proved in the case of salts without making a single quantitative experiment. If two different quantities of the acid A are neutralised with the requisite amounts of the base B, it is easily shown that the two neutral products remain neutral when they are mixed. But this is possible only if the ratio is independent of the absolute quantity. If, for example, a larger quantity of acid requires more than the proportional amount of base, the mixture of the neutral salts will be acid, since their sum corresponds to a larger quantity of acid, and has been added to the quantity of base corresponding to the smaller quantities of acid. The further fact that a neutral salt remains neutral when it is subdivided or put together, proves that the neutralising or combining ratio is independent of the absolute quantity.

It has also been found experimentally, that a neutral salt remains neutral whether it is warmed, electrically charged, exposed to light, or subjected to other physical influences. We may therefore conclude that the ratio is not affected by any of these agencies, since the part in excess would be immediately recognisable by its reaction.

These facts and considerations prove the validity of the law of constant proportions, but they throw no light on the numerical value of the ratios. For this quantitative experiments are necessary.

Chemical Equivalents.—When two different neutral salts are caused to react (the occurrence of the chemical process can frequently be observed), the neutrality is preserved. This apparently "self-evident" fact has unexpected and far-reaching consequences.

Suppose the one salt to be formed from the acid A_1 and the base B_1, the letters representing also the weights of the acid and base. The second salt, formed from the acid A_2 and the base B_2 is added to it until the chemical action (recognisable in some suitable manner) is at an end. Two new salts result, identical with those formed by the direct action of A_1 on B_2, and of A_2 on B_1. Both salts are neutral.

This proves that the acid and the base are in the same proportion in them as in direct neutralisation. Although these proportions were not directly introduced during the reaction, they were present, *i.e.* they were conditioned by the other ratios. If therefore A_1 is neutralised with B_1, and A_2 with B_2, and the two salts are mixed in such proportions that A_1 and B_2 are in the right proportion for salt formation, A_2 and B_1, which remain, are also in the right proportion. For if they were in any other proportion; the excess of acid or base would be shown by the disappearance of neutrality.

As the same experimental result is obtained in whatever order the salts are combined, the following general law is reached.

If we start with an arbitrary quantity of an acid A_1, and find the quantities of different bases B_1, B_2, B_3 . . . which form neutral salts with A_1, and if we find the quantities of different acids A_2, A_3, A_4 . . . which form neutral salts with the quantity of the base B_1, each quantity A_1, A_2, A_3 . . . . forms a neutral salt with each of the quantities B_1, B_2, B_3. . . .

If A and B are called the equivalent weights of the acids and bases, the law can be stated more briefly. Acids and bases combine to form neutral salts only in the ratio of their equivalent weights.

It must be remembered that the quantity A_1 to which all the others are referred, was arbitrarily chosen. The numbers are only relative since the choice of a different quantity of A_1, or of any other acid or base, would lead to a different set of figures. But they would be proportional to the other set, and the law would hold for these values. In determining equivalent weights we must agree upon an arbitrary initial value, exactly as in the case of the arbitrary unit of length or of mass.

The above remarkable reasoning was developed by J. B. Richter about the end of the eighteenth century, but remained unnoticed by his contemporaries. Its significance was recognised only in our own times, and not always fully appreciated even then.

Here, also, we find the explanation of the fact that the existence of a quantitative law was recognisable without quantitative experiments. It depends, as before, on the circumstance that deviations from the definite proportions required by the law can be recognised by means of the action of even slight excess of acid or base on vegetable colours. At the same time there remains the other circumstance, that the existence of the quantitative law can be deduced, but not the numerical values of the constants. Similarly, the impossibility of perpetual motion indicates the existence of a quantitative law; but special investigations were necessary for the determination of the coefficients of transformation, and the proof of the law was independent of a more or less accurate knowledge of these coefficients.

The Law of Combining Weights.—The law of equivalent weights is restricted to neutral salts, because the experimental basis, the preservation of neutrality, is obviously only applicable to them. The question is, whether there is not a more general experimental basis for a correspondingly wider law.

Such a basis does exist. It consists in the fact that pure compound substances form chemical compounds without residue, just like simple substances. Further, there is the general fact, already made use of in the case of salts, that the same substance can be produced in different ways, so long as the requisite elements take a suitable part in the reactions employed. It does not matter whether the salt A_1B_1 is made directly from the acid A_1 and the base B_1, or by the interaction of the salts A_1B_2 and A_2B_1; the nature, and therefore the composition, of the salt remains the same. If the same result is obtained in different ways, it follows that these ways are not independent, but are limited by definite regularities or are related to one another. Otherwise the different ways would lead to different results. This is a general principle of extensive applicability in experimental sciences, and is the foundation of all the applications of the two fundamental laws of energetics.

In the present instance, the circumstance that the same substance can be obtained by different methods, proves that a definite law is involved. The precise form of the law is obtained if we consider what are the characteristics of these different methods. The simplest case will make this plain.

Suppose three substances A, B, and C, capable of forming binary compounds AB, AC, and BC, and also the ternary compound ABC. Make the ternary compound by the union of AB with C; then make it from AC and B. In both cases the same substance ABC is obtained, in which the components are in a fixed ratio; it follows that the same ratios must exist in the binary compounds. If this is not so, ABC could not be formed from AB and C without the separation of the excess of either A or B. The same is true for the formation of ABC from AC and B, and from BC and A. For all these relations to hold at the same time, the three substances A, B, and C must combine in fixed ratios, which depend only on the substances themselves and not on the kind of compound into which they pass.

The same proof holds for a fourth substance D, or for any additional number. From this we obtain the following general law, the specific ratios being called the combining weights of the given substances:

Substances unite only in the ratio of their combining weights.

What was said regarding the numerical values of the equivalent weights of acids and bases applies equally to combining weights. As the values are relative, some unit has to be chosen. And as was also the case with the units of weight and mass, unanimity was not at first attained on the question of the choice of a unit.

The experimental basis for the deduction of the law of combining weights is found in the uncertainty, already mentioned on p. 110, whether the substances now regarded as elements are so in reality, or are merely compounds which have hitherto withstood decomposition. If one single reaction was known, in which a residue of any one component remained over, it would be a proof of its non-elementary nature. Further than this, Berzelius (1810) and Stas (1867) made special experiments, in order to test the law in very delicate reactions more exactly than is possible in direct determinations of combining weights. Berzelius, for example, oxidised lead sulphide to lead sulphate, and tested in the liquid for excess of lead or of sulphuric acid, but found neither of them. The ratio of sulphur to lead in the sulphide is therefore exactly the same as in lead sulphate. He performed a similar experiment with barium sulphite, which he oxidised to sulphate. Stas reversed the process, reducing silver chlorate, bromate and iodate to the corresponding halogen compounds and showed that no excess of either silver or of halogen was recognisable. As these reactions are extremely delicate, and in the form in which Stas performed them were made still more so, the proof was exact to 1 in 10,000,000. These examples were chosen solely on account of the accuracy with which deviations could be detected; we may therefore generalise the conclusion in accordance with the laws of scientific induction, and state that the law of combining weights is so exact that deviations from it are below the limit of measurement.

It should be noticed that these tests of the law are only an appropriate extension of the idea of pure substances. As explained on p. 55, a pure substance undergoes a change of state without the residue differing in any respect from the original substance. Here we have the same definition, extended from simple change of state to transformations of all kinds, and to chemical reactions in particular. The law of combining weights is thus a consequence of the idea of pure substances: we cannot define a pure substance as one which undergoes complete transformation without the residue changing, and not introduce by implication the law of combining weights.

The Law of Multiple Proportions.—A special case arises when a compound unites with an element which it already contains. The law of combining weights applies both to the quantity of that element already present in it and to that with which it unites; they are equal and the final compound contains double the amount of that element. If the process can be again repeated, a product containing three times the combining weight of that element will be obtained. The same can occur with still higher stages of combination, and also with other elements in the compound.

The result may be summarised as follows: elements can combine to form compounds not only in the simple ratios of their combining weights, but also in multiples of them. The multiples must be integral multiples of the simple combining weight.

If two elements A and B can unite to form various compounds, the latter must be represented by a formula of the form $mA + nB$, where m and n are whole numbers, and A and B are the combining weights. In general, all chemical compounds are capable of representation by a formula of the type $mA + nB + pC + qD + \ldots\ldots$, the coefficients being whole numbers. The whole of chemical experience is in general agreement with this law.

The first examples of this law were discovered simultaneously and independently by Dalton and Wollaston at the beginning of the nineteenth century. In text-books it is known as the Law of Multiple Proportions.

The Atomic Hypothesis.—So far the stoichiometric laws are simply an expression of ascertained facts, and possess all the certainty of inductive laws. With a view to render their general relations more clearly and to facilitate further conclusions, a method of representation has been adopted, from which the laws can be deduced. This representation is incapable of proof, except as to its conclusions; as it is impossible to prove that no other representation can lead to the same consequences, it is obviously impossible to prove it to be correct. But it is convenient, if it permits the consequences to be developed in a clear and easy manner, thus facilitating further applications of the laws.

Such representations are called hypotheses; they always consist in applying known regularities to less known regions in which similar regularities have been noticed. Since mechanical science is the best known of all subjects theoretically, it has hitherto usually provided the material for hypotheses. The present case is no exception, for it represents chemical regularities on the assumption of certain mechanical properties possessed by the substances concerned.

This assumption is, that matter does not completely occupy space, but consists of small particles, which, by their union, form what appears to us as matter. These small particles are called atoms. The atomic hypothesis dates from the ancient Greek philosophers, and has always played a part during the whole history of the science. Until the beginning of the nineteenth century it remained merely qualitative and indefinite; but Dalton (1803) essayed to apply it quantitatively and obtained satisfactory results.

The first question he asked was whether the atoms of a given substance are all exactly alike, or merely similar like grains of sand.

If the latter, it should be possible to prepare two samples of a substance, say water, with slightly different properties, just as sand can be separated into a coarser and a finer part by means of a sieve. At first sight this seems the case, for river water, spring water, and sea water are similar but not quite the same. Closer investigation shows the contrary. They are different because they are not pure, *i.e.* are not water and nothing else. When they are completely freed from foreign substances they all yield water which is so alike in every respect that no recognisable difference can be detected.

From this Dalton concluded that the atoms of any one pure substance are exactly alike. This consideration, which is the necessary basis for the deduction of the laws of stoichiometry from the atomic hypothesis, is the figurative equivalent of the property of transformation without leaving a residue (p. 114), which as a base for the law is entirely free from hypothesis.

Dalton made the further assumptions that chemical compounds are formed by the union of atoms of the components or elements in fixed numbers, and each compound contains the atoms of its elements arranged in a definite manner.

The stoichiometric laws can be deduced directly from these assumptions. Since the atoms of each element are exactly alike, their weights are the same. And as atoms can only unite in whole numbers, the proportion by weight of the elements in a compound is given by the product of the number of atoms of the element present and the weight of a single atom. This is the law of combining weights, which, as already explained, embraces all the other laws. The combining weight thus becomes the (relative) atomic weight.

In consequence of the great simplicity of this method of representation, Dalton's atomic hypothesis has not only been used to assist beginners in gaining a knowledge of the facts of chemistry, but is the predominant method of scientific representation. It must be admitted that, so far, it has always been possible to frame the hypothesis in such a way as to represent all other chemical relations in terms of it. Indications are not wanting that the limit has almost been reached, and the opinion that it is inadequate in many respects is gaining ground.

Although most of the subjects treated in this book can be discussed without making other than occasional use of the atomic hypothesis, nearly the whole of our present nomenclature has developed on the lines of this hypothesis; and to attempt to do without it would entail the creation of a new nomenclature. For this reason the old names will still be used, involving a formal retention of the hypothesis, but the tendency of the book is towards a direct statement of the facts and of the laws deducible from them, with the object of placing their general bearings in a clearer light; further, a more correct estimate of the phenomena can be obtained by the exclusion of extraneous matters.

The Table of Elements.—The only way of learning whether a given substance is simple or compound is to assume that it is compound and apply all known methods to effect its decomposition.

If the products we obtain always weigh more than the substance itself and never less, no matter to what changes it has been subjected, then, provided each change is complete and accompanied by no loss of substance through our imperfect methods, we are constrained to regard that substance as an element.

The conception of an element in the chemical sense is therefore that of an undecomposed, not of an undecomposable substance, and is consequently liable to some extent to change, being specially dependent on the resources of chemical analysis, so that it must remain quite uncertain whether or not the substances called elements have any real title to the simplicity implied in the name.

The number of elements hitherto discovered is about eighty; an exact figure cannot be given, as the record of some substances usually looked on as elements is not yet closed and their claims are therefore doubtful. The following is a list of the undoubted elements[1]:—

Aluminium	Al	Europium	Eu	Molybdenum	Mo	Silver	Ag
Antimony	Sb	Fluorine	F	Neodymium	Nd	Sodium	Na
Argon	A	Godolinium	Gd	Neon	Ne	Strontium	Sr
Arsenic	As	Gallium	Ga	Nickel	Ni	Sulphur	S
Barium	Ba	Germanium	Ge	Nitrogen	N	Tantalum	Ta
Bismuth	Bi	Glucinum	Gl	Osmium	Os	Tellurium	Te
Boron	B	Gold	Au	Oxygen	O	Terbium	Tb
Bromine	Br	Helium	He	Paladium	Pd	Thallium	Tl
Cadmium	Cd	Hydrogen	H	Phosphorus	P	Thorium	Th
Cæsium	Cs	Indium	In	Platinum	Pt	Thulium	Tu
Calcium	Ca	Iodine	I	Potassium	K	Tin	Sn
Carbon	C	Iridium	Ir	Praseodymium	Pr	Titanium	Ti
Cerium	Ce	Iron	Fe	Radium	Ra	Tungsten	W
Chlorine	Cl	Krypton	Kr	Rhodium	Rh	Uranium	U
Chromium	Cr	Lanthanum	La	Rubidium	Rb	Vanadium	V
Cobalt	Co	Lead	Pb	Ruthenium	Ru	Xenon	Xe
Columbium	Cb	Lithium	Li	Samarium	Sm	Ytterbium	Yb
Copper	Cu	Magnesium	Mg	Scandium	Sc	Yttrium	Y
Dysprosium	Dy	Manganese	Mn	Selenium	Se	Zinc	Zn
Erbium	Er	Mercury	Hg	Silicon	Si	Zirconium	Zr

It is presumed that the reader, from his knowledge of descriptive chemistry, is already sufficiently acquainted with the nature and properties of the chemical elements, so that these may be passed over here. Attention need only be drawn to one point, viz. that by far the greater number of the elements are metals, the similarity of whose properties forms one of the arguments which speak in favour of the assumption that the elements are substances of the same order.

To the names of the elements in the above table are affixed their

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[1] In consequence of the latest researches of Ramsay and his co-workers, the elementary nature of the substances hitherto regarded as elements and so termed above is doubtful. But until the new relations have been completely cleared up from a scientific point of view, there is no other course than to retain the old method of representation, with a repeated warning of the provisional character of our determination of elements.

abbreviated symbols. Such symbolic representations have been in vogue in chemistry from the earliest times, when in particular the metals obtained the signs of the planets. They had at first only a qualitative significance, and stood simply for the name of the substance. With the discovery of the law of combining weights, however, they received an extended, quantitative, meaning, as they then had to represent a combining weight of the substance in question. Dalton, immediately after propounding the atomic hypothesis, elaborated such a system of symbols, which, however, consisted of arbitrary signs, and consequently made great demands on the memory. Berzelius was the first to invent a really practical symbolic notation, namely that in which the first one or two letters of the names of the elements were used to represent their atoms.

Chemical Formulæ.—Chemical compounds are symbolised by writing the elementary symbols alongside each other. If several atoms of an element are present in the compound, its symbol is in general not repeated, but has merely the number of the atoms affixed to it, commonly in the place of the mathematical index, more unusually prefixed as a factor. In complex formulæ a great saving of space is thus effected.

The significance of chemical formulæ is not exhausted by the indication of the nature and number of the atoms. In the first place, as a knowledge of the relative combining weights is postulated, they give us complete information regarding the relative masses of the elements in the compound. Again, it is sought through them to give a representation of the more or less intimate relations in which the atoms stand to each other in the molecule. With this intention we write constitutional formulæ, in which these relations are exhibited by the relative positions of the symbols.

Estimation of Combining Weights.—According to a preceding section (p. 115) there exists for each element a definite number, which either by itself or when multiplied by a whole number determines the mass and weight of that element that enters into its compounds. This number, the combining-weight, can only be determined relatively, *i.e.* that of one element must be arbitrarily fixed, those of the other elements being referred to this value.

Considered from the point of view of the atomic hypothesis, these numbers are the relative masses or weights of the atoms, and are therefore usually called atomic weights. We may use in the following pages the hypothetical name "atomic weight," as it is now employed in all branches of chemical literature and as no grave error is likely to arise from its use.

The determination of the relative combining or atomic weights was the most important task experimental chemistry had to undertake after the discovery of the fundamental laws of mass. For if these constants were once correctly determined, it became possible to calculate the relations of mass in all chemical compounds with this same degree of accuracy after the relative numbers of the different atoms had been ascertained by an analysis of only approximate correctness.

At first it was practically Berzelius alone who devoted himself to this task, and executed it in a comprehensive way with a degree of certainty and accuracy quite extraordinary for his time. His numbers therefore enjoyed the greatest confidence, especially on the Continent. In England somewhat different numbers were in use, in consequence of a hypothesis which will be discussed later. When these numbers, however, were subjected to a revision by Turner, the values of Berzelius were found to be confirmed in the most striking manner, so that the confidence in the accuracy of the latter reached at this time its highest point.

Meanwhile the most careful experimenters, in the course of the analysis of organic compounds containing only carbon and hydrogen, found numbers which made the sum of the components appear greater than the quantity of substance taken. As, in the analysis, carbon is weighed as carbon dioxide, and hydrogen as water, there remained nothing but to conclude that the quantity of the element in question which the one or the other contained had had a wrong value assigned to it in the calculation. Researches of Liebig and Redtenbacher, Dumas and Stas, Erdmann and Marchand, which were made to test this, all went to prove that Berzelius in his determination of the atomic weight of carbon had made a considerable error, one of about two per cent.

This wholly unexpected discovery (1841) created a perfect panic amongst chemists. The height of confidence formerly felt in the numbers of Berzelius was now equalled by the depth of distrust conceived for them, and this distrust was considerably enhanced by the position assumed by Dumas with regard to the question. An active revision of Berzelius's numbers at once commenced, the result of which was to show that this error was by far the largest, in fact almost the only one he had committed; the numerous redeterminations all confirmed the correctness of the other values found by this conscientious experimenter.

Since then revisions and redeterminations of the atomic weights have been steadily in progress. Thrice, however, they have received a special impulse. First, a hypothesis advanced by Prout and Meinecke stating that all atomic weights were multiples of that of hydrogen incited to a great number of extremely accurate researches, in particular to those of Stas. Again, the relation discovered by Mendelejeff and Lothar Meyer between the masses and the other properties of the atoms occasioned many investigations, for in particular cases the general relation seemed not to hold, and as a probable cause of this was the inexact determination of the atomic weights, a revision of these became necessary. Finally, the circumstance that a systematic recalculation of the existing determinations of the combining weights about twenty-five years ago, directed attention to the incomplete nature of many of the determinations, and led to renewed researches. Th. W. Richards has rendered great service in this work.

Unit of Combining Weight.—As we can at present determine the values of the atomic weights only relatively, we have in the first place to fix the unit to which they may all be referred, *i.e.* the atomic weight of one of the elements must be arbitrarily fixed equal to a certain number. Dalton adopted hydrogen as his standard, as its atomic mass was the smallest of all. Berzelius subsequently abandoned this unit for the following practical considerations. There are very few hydrogen compounds that are capable of being analysed with exactness, so that the ratio between the atomic weight of hydrogen and that of other elements can only be determined for the most part indirectly. Oxygen, on the other hand, forms very suitable compounds with nearly all the elements, and so Berzelius chose it as his standard substance, setting its atomic weight not equal to unity, but to 100, so that the other atomic weights might be of convenient magnitude. Later on, chemists returned to Dalton's unit, because hydrogen had become in other respects a standard substance in the science. A practical difficulty has, however, arisen from this, viz. that all the values of atomic weights which have been determined with respect to oxygen—and that is the great majority—must be calculated by the aid of the ratio Hydrogen : Oxygen. Unfortunately this ratio was until lately by no means accurately known; the possible error in it amounted to much more than the error in a large number of atomic weights of elements compared to that of oxygen, so that by this method of calculation the results were affected with unnecessary inexactness.

It is therefore most practical to formally retain Dalton's unit, but really to return to that of Berzelius by arbitrarily setting the atomic weight of oxygen, which is very approximately sixteen times that of hydrogen, equal to 16.

The ratio between oxygen and hydrogen is now known with sufficient accuracy, thanks to a series of excellent researches. But the determination of this ratio is so difficult that many other atomic weights could have been determined with less error with the same expenditure of time and skill. This drawback is not removed, and will again become apparent when work on the other elements has made sufficient advance.

It was therefore not without good reason that the German Chemical Society in 1898 resolved to recommend its members to adopt $O = 16{\cdot}000$ as the unit for calculation. Since then an international agreement to the same effect has been arrived at.

This is the same mode of procedure that recommended itself as the only practical one in fixing the metric unit of length. The metre was originally intended to be a ten-millionth part of the earth's quadrant. The determination of this value, however, by geodetic measurement is susceptible of much less accuracy than the process of making copies of this length once it is determined, so that we run the danger of getting a sensibly different metre at every new measurement of arc. It was therefore agreed to accept the original measure of length kept in Paris and constructed in the above way as the real metre, and to give up its relation to the earth's quadrant altogether.

Examples.—Of the numerous researches that have been undertaken with a view to fixing the atomic weights of the various elements only a few can be mentioned here. But at least the most important of the methods employed will be illustrated by examples.

The atomic weight of hydrogen when that of oxygen is fixed at 16 is approximately 1. The first of the more exact determinations was carried out in 1819 by Berzelius and Dulong according to a method which has since been retained by almost all other investigators. It consists in leading pure, dry hydrogen over red-hot copper oxide. The hydrogen takes up oxygen from copper oxide to form water, which is then collected in suitable vessels, the last particles of water vapour being held back by dehydrating agents such as sulphuric acid or phosphorus pentoxide.

In the three experiments 30·519 g. of water were obtained. The copper oxide, which was weighed before and after the experiment, lost 27·129 g. This represents the oxygen contained in the water; the quantity of hydrogen therefore is $30{\cdot}519 - 27{\cdot}129 = 3{\cdot}390$ g. In water we assume that there are two atoms of hydrogen to one of oxygen; if the mass of the latter is 16, the following proportion will hold, [H] being the atomic weight of hydrogen,

$$16 : 2[\mathrm{H}] = 27{\cdot}129 : 3{\cdot}390,$$

or

$$[\mathrm{H}] = \frac{16 \times 3{\cdot}390}{2 \times 27{\cdot}129} = {\cdot}9997.$$

Similar experiments with similar results were later performed by Dumas and by Erdmann and Marchand. All these investigators concluded from their measurements that the ratio H : O is 1 : 16·00.

But when later Stas (1860) gave out, on the ground of some unpublished work, that he believed the ratio to be too high L. Meyer recalculated the old data and found 15·96 for oxygen when H = 1. This value received confirmation from Regnault's (erroneous) estimation of the density of the gases, from which the combining weights can be obtained in a manner which will be described later on.

In consequence the use of atomic weights referred to O = 15·96 extended, while on the other hand the uncertainty of this figure was emphasised and the arbitrary unit O = 16·00 was recommended. To compose the difference by finally settling the important constant numerous investigations have been made since 1887, and very different methods have been employed. Cooke and Richards changed Berzelius's process by weighing the hydrogen and the water. Similarly, Keiser (1888 and 1899) weighed the hydrogen in the form of palladium hydride. Rayleigh (1889) weighed both gases separately, and determined the ratio by combining them a little at a time in a eudiometer. He also used for the calculation the volume ratio as found by Scott. Noyes (1888 and 1906) admitted hydrogen to an evacuated bulb, which contained copper oxide, found the increased weight due to hydrogen, then expelled the water and thus obtained its weight. Dittmar and Henderson (1890), also Leduc (1892), repeated the experiments of Berzelius, taking into account the sources of error which had been discovered. Morley weighed the two gases separately (the hydrogen in palladium) and then the water (1895). He also in a masterly research determined the densities and the volume ratio. Thomsen determined the ratio in which ammonia and hydrochloric acid unite, and on the basis of the values for chlorine and nitrogen found by Stas, he calculated the value for hydrogen (1894). In another series of experiments he determined the weight of hydrogen liberated by the action of aluminium on potassium hydroxide, burnt the hydrogen and weighed the water (1895). Lehfeld compared hydrogen and silver by electrolysis. With O = 16, the following have been found for hydrogen. Cooke and Richards 1·0069, Keiser 1·0031 (later 1·0076), Rayleigh 1·0072, Noyes 1·0065, Dittmar and Henderson 1·0087, Leduc 1·0059, Thomsen 1·000 and 1·0082. Morley's determinations are to be regarded as the most reliable of all the recent work, and from them H = 1·00762. This is the value we shall adopt for future use; for many purposes it can be rounded off to H = 1·01.

The Silver Method.—A good example of a somewhat more complicated mode of procedure for the determination of atomic weights is to be found in the method, again given by Berzelius, for chlorine, potassium, and silver, and it was afterwards employed by several chemists, in particular by Marignac, Stas and Richards.

Potassium chlorate, $KClO_3$, is decomposed by heat into $KCl + 3O$. Stas, taking in such an experiment 127·2125 g. chlorate, found 77·4023 g. potassium chloride in the residue, consequently 49·8102 g. oxygen had been driven off. Now as three atoms of oxygen are contained in the potassium chlorate, we can set the following proportion, where [KCl] is the formula-weight of potassium chloride KCl:

$$3 \times 16 : [KCl] = 49{\cdot}8102 : 77{\cdot}4023,$$
$$[KCl] = 74{\cdot}59.$$

The formula-weight of potassium chloride is therefore 74·59, *i.e.* the sum of the atomic weights of potassium and chlorine is equal to this number.

To get the separate values from this the combining-weight of silver chloride was obtained by its aid. For this purpose a known quantity of potassium chloride was precipitated by excess of silver solution and the silver chloride washed and weighed. In this way Marignac (1846) obtained from 14·427 g. potassium chloride 27·732 g. silver chloride, so that the combining-weight of the latter may be found from the proportion

$$74·590 : [AgCl] = 14·427 : 27·732$$

to be

$$[AgCl] = 143·37.$$

Lastly, the ratio of chlorine to silver in silver chloride was determined by the transformation of a known weight of silver into silver chloride, the weight of which was also observed. This transformation can be brought about in various ways; we can heat the silver in a stream of chlorine, when it goes directly into silver chloride, or we may first dissolve it in nitric acid so that it becomes silver nitrate, which is then converted into silver chloride by precipitation with hydrochloric acid, ammonium chloride, or any other suitable compound of chlorine. The same ratio between silver and silver chloride is always obtained, no matter which process we adopt. From such experiments I select one by Stas, who found that 101·519 g. silver gave after heating in a stream of chlorine 134·861 g. silver chloride. As the formula-weight of the latter was found above equal to 143·37, we get the atomic weight of silver from the proportion

$$143·37 : [Ag] = 134·861 : 101·519,$$
$$[Ag] = 107·93.$$

The atomic weight of silver is consequently $Ag = 107·93$. From this follows further, since $AgCl = 143·37$, that the atomic weight of chlorine is $143·37 - 107·93 = 35·44$. Lastly, if we subtract this value $Cl = 35·44$ from the number obtained in the first series, $KCl = 74·59$, the atomic weight of potassium follows as $K = 39·15$.

For the three alkali metals Stas employed the method of silver titration, originally worked out for quite another purpose by Gay-Lussac, and used for the first time by Pelouze (1845) in atomic weight determinations.

If a silver solution be added in small quantities at a time to the solution of a chloride, we can easily tell the moment when all the chlorine has gone into silver chloride by a further drop of silver solution producing no cloudiness in the liquid which has been made clear by shaking and allowing to stand.

For example, 10·5249 g. sodium chloride were weighed out; this required a quantity of silver solution which contained 19·4160 g.

silver dissolved in nitric acid. If [NaCl] be the combining-weight of sodium chloride, it follows, as 107·93 is that of silver, that

$$[\mathrm{NaCl}] : 107{\cdot}93 = 10{\cdot}5249 : 19{\cdot}4160,$$
$$[\mathrm{NaCl}] = 58{\cdot}50.$$

In this way, then, the value for the chloride is obtained; if the atomic weight of chlorine, 35·44, be subtracted from this, then we have that of sodium, $Na = 23{\cdot}06$. In a similar way that of lithium was found to be $Li = 7{\cdot}030$.

For nitrogen, silver was transformed into silver nitrate. In one such experiment 77·2684 g. silver gave 121·6749 g. nitrate, whence, according to the proportion

$$[\mathrm{AgNO_3}] : 107{\cdot}93 = 121{\cdot}6749 : 77{\cdot}2684,$$
$$[\mathrm{AgNO_3}] = 169{\cdot}95,$$

the combining-weight of silver nitrate $AgNO_3$ is 169·95, and from this, by subtracting $Ag = 107{\cdot}93$ and $3O = 48{\cdot}00$, we get the atomic weight of nitrogen $N = 14{\cdot}02$.

It must be explicitly understood that the figures given above are the results of actual experiments, and are therefore liable to error. The most probable values are given in the following comprehensive review.

The Combining-Weights of the Elements.—The experiments described above give examples of the different general methods adopted for the determination of atomic weights. In the following pages short notices of the methods employed in each case and the most accurate of the numbers obtained are given for all the elements.

1. *Aluminium.*—Berzelius in 1812 obtained the number $Al = 27{\cdot}32$ by igniting aluminium sulphate. With this result derived from a single experiment at the very beginning of such researches the chemical world was content for over thirty years, till Tissier (1858), and after him many others, determined the constant anew. The number at present recognised as correct was obtained by Mallet (1880), who from the ignition of crystallised ammonium alum ($2NH_4AlS_2O_812H_2O : Al_2O_3$) found $Al = 27{\cdot}12$, by titration of aluminium bromide with silver solution $Al = 27{\cdot}11$, by combustion of the hydrogen evolved by weighed quantities of aluminium from potash ($2Al : 3H_2O$)$Al = 27{\cdot}05$, and by measurement of the hydrogen got in the same reaction $Al = 27{\cdot}04$. Thomsen (1895) found by the hydrogen method $Al = 26{\cdot}98$; Baubigny (1883) converted the sulphate into oxide and obtained $Al = 27{\cdot}06$. $Al = 27{\cdot}1$ may be accepted as the most probable value of the atomic weight.

2. *Antimony.*—The atomic weight of this element was till 1856 only roughly known. By reduction of natural antimony glance from Arnsberg by means of hydrogen ($Sb_2S_3 : 2Sb$) Schneider (1856) obtained $Sb = 120{\cdot}5$, while Rose (1856) from the analysis of $SbCl_3$

found Sb = 120·6. It is true that Dexter at the same time got higher numbers by oxidation of antimony to tetroxide by means of nitric acid ($2Sb : Sb_2O_4$), these being apparently confirmed by Dumas's titration experiments with antimony chloride and silver solution (1859); but a thorough investigation by Cooke (1880) proved that Schneider's number was correct. The error in the determinations of Dumas lies in the fact that such easily decomposable chlorides as antimony chloride are scarcely ever to be obtained in a state of purity. The least trace of aqueous vapour forms oxychloride, while hydrochloric acid escapes, and the oxychloride cannot be completely separated from the chloride by distillation. Consequently the preparation contains too little chlorine and the atomic weight comes out too high.

The experiments of Cooke consisted of syntheses of antimony sulphide ($2Sb : Sb_2S_3$), determinations of the bromine in antimony bromide ($SbBr_3 : 3Agbr$), titrations of antimony bromide with silver solution ($SbBr_3 : 3Ag$), and determinations of the iodine in antimony iodide ($SbI_3 : 3AgI$). The mean is Sb = 120·2. Later experiments of Schneider (1880), also on the sulphide, gave Sb = 120·4.

This number has since been repeatedly confirmed. Experiments on a new principle were performed by Pfeifer (1881) and Popper (1886). According to Faraday's law of electrolysis (see below), the same current separates from different electrolytes equivalent quantities of their components. If a current, therefore, be passed through a silver and an antimony solution successively, the deposited quantities of the metals must be in the proportion of their "equivalents," *i.e.* in the proportion Sb : 3Ag. In this way Sb = 120·7 was found. A series of experiments by Bongartz (1883), in which the sulphur in antimony sulphide was transformed into barium sulphate, yielded the value Sb = 120·6. Friend and Smith (1901) heated tartar emetic in a current of hydrochloric acid, and weighed the residual KCl; $C_4H_4KSbO_7 : KCl = 1 : 0·23048$. This gives Sb = 120·37, which is probably very near the correct value. We put Sb = 120·4.

3. *Argon.*—This remarkable constituent of the atmosphere forms no known compounds: its probable formula-weight must be deduced from its gas density. The value for this given by its discoverers, Ramsay and Rayleigh (1895), lead to A = 39·88; later more accurate measurements on carefully purified material by Ramsay and Travers (1900) gave the density 19·88, from which A = 39·96.

4. *Arsenic.*—This element has been the subject of but few researches. An interesting method was employed by Berzelius (1818), who heated arsenic trioxide with excess of sulphur. The loss of weight from the escaping sulphur dioxide ($2As_2O_3 + 9S = 2As_2S_3 + 3SO_2$) yields the required relations. The number obtained by Pelouze (1845) and Dumas (1859) by titration of arsenic trichloride with silver solution, was As = 75·0. Later investigations

by Wallace (1859) and Kessler (1855-61) by various methods are not free from error. Hibbs (1896) heated sodium pyroarsenate in a stream of hydrochloric acid and weighed the sodium chloride. It gave $Na_4As_2O_7 : NaCl = 1 : 0{\cdot}6610$. Ebaugh (1901) converted silver arsenate into silver chloride in a current of hydrochloric acid, and reduced the chloride to silver by means of hydrogen. He repeated these experiments with lead arsenate and hydrochloric acid and hydrobromic acid. The ratios were $Ag_3AsO_4 : 3AgCl : Ag = 1 : 0{\cdot}92944 : 0{\cdot}69966$, and $2Pb_3As_2O_8 : 3PbCl_2 : 3PbBr_2 = 1 : 0{\cdot}92731 : 1{\cdot}22442$. From this and the best of the older results As = 75·02.

5. *Barium.*—The atomic weight of barium was determined first by Berzelius (1811) from the transformation of the carbonate into the sulphate ($BaSO_4 : CO_2$), later by him and many others (Turner, 1829; Pelouze, 1845; Marignac, 1848 and 1858; Dumas, 1859) by means of the precipitation of the chloride by silver solution. Besides these processes there are a few other less exact methods which need not be mentioned. The older work is quite eclipsed by the researches of Richards (1893) who determined with great exactness the ratio of barium chloride and barium bromide to silver. From his work Ba = 137·37.

6. *Bismuth.*—For the atomic weight of this metal an incorrect value has almost always been in use. The experiments of Lagerhjelm (1816) and Gmelin (1843) had given too high results, and though Schneider (1851) by oxidation of the metal had fixed the value rightly at 208, yet on the authority of Dumas, who obtained (1859) too high results by the method of silver titration, the wrong figures were used almost exclusively. Only recently have they been given up, as both Löwe (1883), by oxidation of the metal, and Marignac (1883), by transformation of the oxide into the sulphate and by reduction of the oxide to metal in a current of hydrogen, found a smaller number, in agreement with Schneider's determination. This has again been called in question by Classen (1890) who from the conversion of metal into oxide by heating the nitrate, obtained Bi = 209. Schneider repeated his work and again found 208. This number is confirmed by a new investigation of Gutbier (1908). He oxidized very pure bismuth to the trioxide and found $2Bi : 3O = 0{\cdot}89656 : 0{\cdot}10344$, which gives Bi = 208·0.

7. *Boron.*—To determine this atomic weight Berzelius (1824) established the percentage of water in crystallised borax, whence follows B = 11·01. With this number we had to be content until 1892, as some analyses of the chloride and bromide by Deville (1859) gave numbers which did not sufficiently agree among themselves. Then a number of new determinations were made. Abrahall (1892) analysed boron bromide, Ramsay and Aston (1893) estimated the percentage of water in borax, and converted it into sodium chloride and silver chloride. Rimbach (1893) titrated borax alkalimetrically

with methyl orange as indicator. Armitage (1898) determined the water in borax, and the ratio of borax to sodium sulphate. Gautier (1899) converted boron sulphide into barium sulphate, boron carbide into carbon or carbon dioxide, boron bromide into silver bromide and the chloride into silver chloride. As mean B = 11·0.

8. *Bromine.*—The older determinations of the atomic weight of bromine by Balard (1826) and Liebig (1826) give too low results, as the material was not free from chlorine. Berzelius obtained a better value by heating silver bromide in a stream of chlorine, when it was converted into silver chloride. Marignac executed a series of experiments $KBrO_3 : KBr$, $KBr : AgBr$, $Ag : Br = AgBr$—exactly similar to that described on p. 124, only bromine occupied the place of chlorine.

Stas, finally, reduced silver bromate to bromide, and determined the ratio Ag : Br in the latter. His experiments were executed on a much larger scale and with much more extensive resources than Marignac's ; yet both series gave quite the same result. Baxter (1906) determined the ratio Ag : AgBr by the synthesis of the bromide and found 0·574453 : 1. Conversion of silver chloride into silver bromide gave AgBr : AgCl = 1·310171 : 1. These agree with each other and with Stas's results. The most accurate value, Br = 79·913, was obtained from the ratio Ag : Br, which was frequently obtained by Richards, Baxter and co-workers in the determinations of other combining-weights.

9. *Cadmium.*—Up to the year 1857 a number was used for the atomic weight of cadmium which rested on a single datum given by the discoverer Stromeyer (1818), but which was afterwards shown to be tolerably accurate. Of the later investigators, von Hauer (1857) converted cadmium sulphate into sulphide by ignition in a current of hydrogen sulphide; Dumas (1859) titrated the chloride with silver; Lenssen (1860) analysed cadmium oxalate; and lastly Huntington (1881) analysed the bromide both gravimetrically and volumetrically by converting it into silver bromide. A later research by Partridge (1890) made no advance, and the estimation of the ratio metal : oxide by heating the nitrate (Morse and Jones, 1892) is open to the objection that complete decomposition of the nitrate by heat is difficult to attain. The same investigators also analysed the oxalate, and applied (1898) a correction for occlusion in the oxide. Bucher (1892) repeated nearly all the methods. Morse and Arbuckle (1898) determined the ratio $CdCl_2 : Cd = 1 : 0·8752$. Lorimer and Smith (1892) electrolytically reduced the oxide, and Hardin (1896) also employed electrolytic methods. Baxter, Hines and Frevert (1905) converted the chloride and the bromide into the silver salts and found $CdCl_2 : 2AgCl = 1 : 1·56365$, $CdCl_2 : 2Ag = 1 : 1·17713$, $CdBr_2 : 2AgBr = 1 : 1·37962$, $CdBr_2 : 2Ag = 1 : 0·79210$. From these, Cd = 112·4, in close agreement with Morse's number.

10. *Caesium.*—The number for this element was first determined

by weighing the silver chloride obtained from a given quantity of caesium chloride. The older experiments of Bunsen (1861) and Johnson and Allen (1862) were made with impure material. More accurate results of Godeffroy (1876) gave 132·6. Richards and Archibald (1903) found AgCl : CsCl = 1 : 1·17401, and Ag : CsCl = 1 : 1·55963. Conversion of caesium nitrate into oxide gave N_2O_5 : Cs_2O = 1 : 2·60693, of the bromide into silver bromide or into silver CsBr : AgBr = 1 : 0·88277, and CsBr : Ag = 1 : 0·50710. This makes Cs = 132·81.

11. *Calcium.*—Although calcium occurs in the earth's crust in greater quantity than any other metallic element, its atomic weight is nevertheless not known with a certainty corresponding to its importance. Berzelius at the very beginning of his researches (1811) performed one single analysis of calcium chloride, and with the number calculated from this, which also contained a clerical error, chemists were satisfied for the next thirty years, when Dumas (1842) made some determinations by igniting Iceland spar ($CaCO_3$: CaO). Thereupon Erdmann and Marchand undertook a long investigation (1842-50), employing various methods, the final result of which was a single faultless experiment on the loss of calcium carbonate when ignited. This gave Ca = 40·0. The uncertainty which exists as to this value is not diminished by a series of experiments made by Dumas (1859), who titrated calcium chloride with silver, as the preparation of the chloride quite free from oxide presents great difficulties, which Dumas does not prove himself to have overcome. Herzfeld (1897) repeated the analysis of the carbonate, but Hinrichsen's (1902) experiments were the first to yield good results. They lead to Ca = 40·12, in close agreement with the analysis of the chloride by means of silver made by Richards (1900).

12. *Carbon.*—The determination of the atomic weight of this element was at first founded by Berzelius on the observation that oxygen does not increase in volume when converted into carbon dioxide; therefore the atomic weight of oxygen is to that of carbon dioxide as the specific gravities of the two gases. This is not, however, strictly correct; the volume of the carbon dioxide is somewhat smaller than that of the oxygen, and a false value thus arose which was only corrected in 1841 by the researches of Liebig and Redtenbacher, of Dumas and Stas, and of Erdmann and Marchand (p. 121). The value C = 12·00 found by these chemists has been confirmed several times by later investigators, *e.g.* by Stas (1849) from the combustion of carbon monoxide, by Roscoe (1882) from the combustion of Cape diamonds, in the same way by Friedel (1885), and lastly by van der Plaats (1885), who burned sugar charcoal, graphite, and paper charcoal. Parsons (1905) calculated from his experiments with glucinum salts (see these) C = 12·007. Therefore we may put with great certainty C = 12·00.

13. *Cerium.*—The determination of the atomic weight of this element has been one of uncommon difficulty. The difficulty lay, not so much in the analytical methods, but rather in the separation of the cerium compounds from those of the other earths which accompany them. It is on account of this circumstance that different chemists, working with equal care, have arrived at very different results.

The oldest determinations by Hisinger (1816) were made at a time when lanthanum and didymium, which always accompany cerium, were not yet discovered. Beringer (1842) was the first to work with anything like pure preparations. He analysed the chloride and sulphate. Later researches by Hermann, Rammelsberg, Marignac, Jegel, Wolf, and Bührig showed that according to the origin and method of purification of the cerium preparations employed, very different atomic weights (between 130 and 140) are obtained. Only recently have Robinson (1884) and Brauner (1885) obtained concordant results with carefully purified material in quite independent researches. The method was that of converting the sulphate into the oxide by ignition, and the result obtained was Ce = 140·2. This concordance seems to have been accidental, for Schützenberger (1895) showed that fractional crystallisation of cerium salts yielded fractions of different colour and different atomic weight. Brauner confirmed this, and determined the atomic weights of the various fractions. Further experiments by Wyrouboff and Verneuil (1897) and by Kölle (1898) were on the change of the hydrated and anhydrous sulphates into oxide. They gave Ce = 139·4 to 138·8. Finally, Brauner and Batek (1903) in a very thorough investigation transformed the sulphate and the oxalate into oxide. The result was Ce = 140·25.

14. *Chlorine.*—The method first employed by Berzelius has already been given on p. 124, and by its means the atomic weight of this element has finally been fixed. The number of investigators, from Berzelius to Stas, who have proved their strength on this task has been very large, the most exact results besides those already mentioned being obtained by Penny (1839) and Marignac (1842-1846). Other methods were, it is true, attempted, but they met with no success. Marignac, for instance, obtained very inaccurate results by heating copper oxide in a stream of hydrochloric acid gas ($CuO + 2HCl = CuCl_2 + H_2O$); and the results of the analysis of a complicated organic compound, by which method Laurent (1842) sought to solve the problem, are just as little worthy of confidence. The ratio Cl : Ag has been recently determined very exactly by Richards and Wells (1905) by direct synthesis of silver chloride. Numerous other results mentioned under other elements, in which a chloride is connected with silver chloride and silver, can be used. There are so many separate determinations that the atomic weight of

chlorine can be very accurately calculated. In addition, Avogadro's principle affords a comparison between chlorine, hydrogen and oxygen; calculation from the synthesis of hydrochloric acid, or from the analysis of silver chlorate seems almost superfluous. The former has been done with great accuracy by Dixon and Edgar (1905) and from it Cl = 36·463, while the value given by Stas is 35·455, and by Richards 35·467. From the relation of chlorine to silver, if Ag = 107·883, Cl = 35·459.

15. *Chromium.*—The atomic weight of this element must be classed with those which have not been quite firmly established by a thorough investigation. Berzelius in 1818 made some analyses of lead chromate and barium chromate, the results of which were much further removed from the truth than was usual with this exact worker. Berlin (1846), who transformed silver chromate into silver chloride and chromic oxide, found the wished-for number with sufficient approximation. Later researches by Morberg (1848), Lefort (1850), Wildenstein (1853), and Kessler (1861), in which different and mostly unsuitable methods were employed, are inferior to the work of Berlin. Siewert (1861) drew attention to a source of error in Berlin's determination, supposed to be caused by the slight solubility of silver chloride in the acid chromic solution from which it was precipitated; by avoiding this he obtained 52·1 instead of Berlin's 52·5. Baubigny (1884) found a value between these two from the transformation of chromic sulphate into chromic oxide by strong ignition. Rawson (1889) decomposed ammonium dichromate by heat, Meinecke (1891) converted silver chromate and ammonium silver chromate into silver chloride, and ammonium chromate into chromic oxide by precipitation with mercurous nitrate and heating the mercurous chromate. The recent work gives a value somewhat smaller than the older one; as a mean Cr = 52·1.

16. *Cobalt.*—A great number of researches have been undertaken on this element, especially for the purpose of deciding whether cobalt and nickel have the same or different atomic weights, and for no other element have different but equally trustworthy investigators obtained such widely divergent results. The chief names are Rothoff (1818), Schneider (1857), Marignac (1857), Gibbs (1858), Dumas (1859), Russell (1863 and 1869), Sommaruga (1866), Winkler (1867), Weselski (1868), Lee (1871), Zimmermann (1886), Remmler (1891), Winkler (1893 and 1894), Hempel and Thiele (1895), Richards and Baxter (1898). The methods applied were very different, and the results vary between Co = 58·8 and 60·6. The question was complicated by Krüss's supposed discovery (1889) of a third metal in nickel and cobalt, which turned out to be an error. Richards and Baxter (1897 and 1899) converted the bromide into silver bromide and by reduction with hydrogen into cobalt, Baxter and Coffin did the same with the chloride. The results were

$CoBr_2 : 2AgBr = 1 : 1{\cdot}71659$, $CoBr_2 : 2Ag = 1{\cdot}01408 : 1$, $CoBr_2 : Co = 3{\cdot}71150 : 1$, $CoCl_2 : 2AgCl = 1 : 2{\cdot}20714$, $CoCl_2 : 2Ag = 1{\cdot}66119$. These data lead to the same result as Hempel and Thiele obtained by reduction of the oxide to metal; Co = 58·98.

17. *Columbium* (*or Niobium*).—The investigation into the nature of this element was attended with considerable difficulties, which Rose, who occupied himself many years with it, did not succeed in overcoming. Blomstrand was the first to get a proper grasp of the subject, and to him we owe the determinations which may be taken as the most exact. The analysis of the pentachloride gave Nb = 94·0. This is in agreement with the mean value found by Marignac by various methods.

18. *Copper.*—Most experiments towards the determination of the atomic weight of this metal have been executed by the reduction of a weighed quantity of cupric oxide heated in hydrogen. Simple as the method appears, yet it is affected with an error having its source in the fact that the spongy reduced copper condenses sensible quantities of hydrogen on its surface, thus increasing its weight. According to this method we have researches by Berzelius (1820), Erdmann and Marchand (1844), Millon and Commaille (1864), and Hampe (1874). The last mentioned further determined the copper in anhydrous copper sulphate by electrolytic deposition. Baubigny (1883) transformed copper sulphate into oxide by ignition.

By quite another method, similar to that adopted for antimony (p. 127), W. N. Shaw (1887) has determined the value in question. He passed an electric current through two solutions, one of which deposited copper and the other silver, and by Faraday's law determined the equivalent and the atomic weights of copper from his results. The number he obtained agrees very closely with that got by the purely chemical methods. Very careful determinations by different methods were made by Th. W. Richards (1886-91). He displaced silver from silver nitrate in cold solution by means of metallic copper, analysed anhydrous copper sulphate, determined the ratio between copper and silver, and between copper bromide and silver bromide. His figure must be regarded as the most satisfactory; it is Cu = 63·60. Since then a less accurate redetermination has been made by Murmann (1906).

19. *Dysprosium.*—This element was discovered by Lecoq de Boisbaudran (1886); Urbain (1900 onward) obtained the oxide in a pure state and found (1907) Dy = 162·5. There is some doubt as to the elementary nature of Dysprosium.

20. *Erbium.*—For this rare element, also, the difficulty of purification is very great. As the substance has become investigated more thoroughly, more and more elements with similar properties have been separated from it, so that we have at present no guarantee that

what we call erbium is really a single uniform substance. The last determinations by Cleve (1880), Hofmann and Krüss (1893), Brauner (1905) gave Er = 167.

21. *Europium.*—The existence of this element was first discovered recently when Lecoq de Boisbaudran (1897) and Demarçay (1896) separated the old samarium into samarium and europium. From the ratio of oxide to sulphate, determined by Demarçay and Urbain and Lacombe (1904), Eu = 152. Further resolution of this element is not improbable.

22. *Fluorine.*—The atomic weight of fluorine had been fixed for a long time before the element itself was known in the free state, a discovery of only recent date. It was only known as a constituent of various compounds, and its existence was inferred from the fact that these compounds are different from all compounds of known elements. For the determination of the atomic weight one method has been used almost exclusively, viz. the conversion of calcium fluoride into calcium sulphate by evaporation with sulphuric acid—$CaF_2 + H_2SO_4 = CaSO_4 + 2HF$. Such experiments were executed by Davy (1812), Berzelius (1818 and 1824), Louyet (1849), Dumas (1859), de Luca (1862) with somewhat varying results, as calcium fluoride is decomposed completely by sulphuric acid only with extreme difficulty. Consequently other compounds, such as sodium, potassium, barium and lead fluoride were used by some investigators. The mean of the good experiments is F = 19·00. This number has been lately confirmed in another way. Christensen (1886) decomposed the compound $(NH_4)_2MnF_5$, which crystallises well, with hydriodic acid ($(NH_4)_2MnF_5 + HI = 2NH_4F + MnF_2 + HF + I$), and determined the liberated iodine volumetrically by means of sodium thiosulphate. The result was the same, F = 19·00. Berzelius and Fremy (1856) converted the fluoride into silver fluoride, but without good result. J. Meyer (1903) acted on calcium oxide with hydrofluoric acid, and found $CaO : CaF_2 = 1 : 1·3932$, from which F = 19·03.

23. *Gadolinium.*—This element was found by Marignac who assigned the atomic weight 156·8. Lecoq de Boisbaudran gives 156·3, Cleve 154·8. All the later results are based on the ratio of oxide to sulphate, [Bettendorf (1891), Benedicks (1900), Brauner (1904), Marc (1904), Urbain (1905)]. These authors, except Brauner and Urbain, confirm the number obtained by Marignac. The true value is probably very near Gd = 157·0.

24. *Gallium.*—Lecoq de Boisbaudran, the discoverer of gallium, determined its atomic weight by igniting ammonium gallium alum, $NH_4GaS_2O_8 + 12H_2O$, when gallium oxide, Ga_2O_3, remained behind. He also converted the metal into oxide. The result is Ga = 69·9.

25. *Germanium.*—The discoverer of germanium, Cl. Winkler,

analysed germanium chloride, $GeCl_4$, by decomposition with sodium carbonate, and volumetric estimation of the chlorine by means of silver solution. From his data we get Ge = 72·5.

26. *Glucinum* (*or Beryllium*).—The analysis of beryllium sulphate is almost the only method. Along with the older and not so exact experiments of Berzelius (1815 and 1826), Awdejeff (1842), Weeren (1854), Debray (1855), Klatzo (1869), we possess very good determinations by Nilson and Pettersson (1880), who performed the analysis of the sulphate in the simplest possible way, namely by strong ignition, when $BeSO_4,4H_2O$ became BeO. These determinations were repeated by Krüss and Moraht (1891), and Parsons (1904) converted the acetyl acetonate and the basic acetate into oxide, and obtained Be = 9·11.

27. *Gold.*—A great many methods have been applied to this element. First of all Berzelius (1813) precipitated a solution of gold with mercury and thus determined the ratio of the atomic weights of the two metals. Javal (1821) obtained quite other numbers by analysis of auric oxide, whereupon Berzelius (1845) determined the ratio between chlorine and gold in a neutral solution of auric chloride, as well as that between gold and potassium chloride, by igniting potassium auric chloride, $KAuCl_4$, in a current of hydrogen. Levol (1850) worked according to a completely different method; he reduced a solution of auric chloride with sulphur dioxide ($2AuCl_3 + 3SO_2 + 6H_2O = 2Au + 3H_2SO_4 + 6HCl$) and determined the ratio between the gold and the barium sulphate precipitated from the solution by barium chloride. G. Krüss, and Thorpe and Laurie have lately (1887) undertaken new determinations by the last method of Berzelius, *i.e.* by the decomposition of double salts of gold, and find in the mean Au = 197·2. This number was left unchanged by a research of Mallet (1889) in which eight different methods were employed.

28. *Helium.*—This element is a gas and is similar to argon. Its discoverer, Ramsay, repeatedly determined its density: the latest determination made by Ramsay and Travers (1900) is probably accurate to less than 1 per cent. It gives He = 3·96.

29. *Hydrogen.*—See p. 123.

30. *Indium.*—The atomic weight of this element has been investigated by its discoverers, Reich and Richter (1864), by Winkler (1867), and by Bunsen (1870). The method principally employed consisted in the oxidation of the metal to oxide. Thiel (1904) used this and other methods, *i.e.* formation of trichloride and tri-iodide from the metal, also conversion of the chloride and bromide into silver chloride and bromide. The results differed in the various methods, from the latter In = 115·0. Mather (1907) repeated the last method and found $InCl_3 : 3AgCl = 1 : 1·94393$, and $InBr_3 : 3AgBr = 1 : 1·58877$; which gives In = 114·9.

31. *Iodine.*—Gay-Lussac (1814), to whom we owe our exact knowledge of this element, determined the ratio in which iodine and zinc combine. Berzelius (1828) decomposed weighed quantities of silver iodide by heating them in a current of chlorine, when they are completely converted into silver chloride, and these experiments were repeated later by Dumas (1859) with exactly the same results. A method similar to that introduced by Berzelius for chlorine (p. 124) was employed by Millon (1843), who transformed potassium iodate into potassium iodide by heating. Marignac (1843) established the ratio between potassium iodide and silver, as well as that between silver and silver iodide.

Stas, finally, analysed silver iodate by decomposition by heat and absorption of the liberated oxygen by means of red-hot copper. He also determined the ratio between iodine and silver, and between iodine and silver iodide. From his experiments, with which those of Marignac are in complete concordance, it results that $I = 126{\cdot}86$. This number has been lately shown by several authors to be about ·5 in 1000 too small, because the silver iodide of Stas and Marignac was contaminated with nitrate. Scott (1902) from the synthesis of silver iodide found $I = 127{\cdot}97$, Ladenburg (1902) found the ratio $AgI : AgCl = 1 : 0{\cdot}610402$, Köthner and Aeuer (1904) repeated both these methods, as also did Baxter (1905); the latter in addition determined $AgI : AgBr$. All these gave concordant results with $I = 126{\cdot}93$.

32. *Iridium.*—From the year 1828 until 1878—for fully fifty years—the scientific world contented itself with a single analysis by Berzelius of potassium iridium chloride. In the last-mentioned year Seubert made a most careful investigation by the same method, the result being $Ir = 193{\cdot}2$. Joly (1890) found the same number.

33. *Iron.*—Berzelius at first (1811) gave a value for the atomic weight of iron which was considerably too low. Stromeyer (1826) and Wackenroder (1844) drew attention to the error, whereupon Berzelius caused a new investigation to be undertaken by Svanberg and Norlin (1846), to which he added some determinations of his own. These, as well as the experiments of Erdmann and Marchand (1844), Maumené (1850), and Rivot (1850), were so arranged that, on the one hand, pure iron was converted into oxide by treatment with nitric acid, evaporation, and ignition, and, on the other hand, pure oxide was converted into the metal by heating in a current of hydrogen. The results, which agree very closely, give $Fe = 56{\cdot}00$. Dumas (1859) analysed the chloride, after which there was no further investigation for many years. Richards and Baxter (1900) found by reduction of the oxide $Fe_2O_3 : 2Fe = 1 : 0{\cdot}69958$. Baxter (1903) analysed ferrous bromide by means of silver and found $FeBr_2 : 2AgBr = 1 : 1{\cdot}74124$, $FeBr_2 : 2Ag = 1 : 1{\cdot}000403$. Accordingly, $Fe = 55{\cdot}86$.

34. *Krypton.*—This gas is like argon and was discovered by Ramsay (1898) in the atmosphere. From the density, Ramsay and Travers (1900) obtained Kr = 81·76.

35. *Lanthanum.*—The atomic weight of this element suffers from the same uncertainty as that of the other rare earths. The numerous investigators who have occupied themselves with its determination will therefore not be named, especially as the methods used were always the same. Until the work of Brauner and Pavlicek (1902) and Jones (1902) moderately accurate results had not been obtained. From the ratio of the oxide to the sulphate and to the oxalate La = 138·9.

36. *Lead.*—Lead takes a prominent place in the history of atomic weights, as being the first element on which Berzelius (1811) exercised his skill. His method consisted in the treatment of metallic lead with nitric acid and subsequent ignition of the nitrate, lead monoxide remaining. He afterwards analysed lead chloride (1818), and reduced lead oxide by means of hydrogen (1830). Turner (1833) converted lead and lead oxide into sulphate, Marignac (1858) and Dumas (1859) titrated lead chloride with silver solution. The value at present in use we owe to Stas, who in two series of experiments converted lead into lead nitrate and into lead sulphate. Baxter and Wilson (1908) precipitated lead chloride with silver nitrate and found $PbCl_2 : 2AgCl : 2Ag = 1 : 1·03111 : 0·77610$, from which Pb = 207·11.

37. *Lithium.*—Very divergent results have been obtained by different chemists in the determination of the atomic weight of this metal. The discoverer Arfvedson (1818) gave Li = 10·3. Vauquelin (1818) then found Li = 9·2, Gmelin (1818) 10·8, Kralovanszky (1827) 10·6; on the other hand, Hermann (1829) 6·1, Berzelius (1830) 6·6, Hagen (1839) 6·5, Mallet (1857) 6·95. Troost, who had before given wrong figures, was the first (1862) to determine the value with approximate correctness. The exact number was then found by Diehl (1862), who decomposed a weighed quantity of lithium carbonate with sulphuric acid and determined the carbon dioxide from the loss of weight of the whole apparatus. Stas, in conclusion, determined by titration the ratio between lithium chloride and silver, and obtained the present number, Li = 7·03.

38. *Magnesium.*—Most of the old determinations were made from the analysis or synthesis of the sulphate, *e.g.* by Berzelius (1812), Gay-Lussac (1819), Scheerer (1846), Svanberg and Nordenfeldt (1848), Jacquelain (1850), Macdonell and Bahr (1852). The last determination is particularly interesting, as being made with a specimen of magnesia obtained from the olivine of a Siberian meteorite. This celestial magnesia proved to be identical with the ordinary terrestrial substance in respect of the atomic weight, as it was in all other properties.

An extensive investigation by Marchand and Scheerer (1850) into the quantity of carbon dioxide contained in natural magnesium carbonate (magnesite from Frankenstein) is unfortunately valueless, as Scheerer nine years later discovered that the material employed contained calcium. The experiments of Dumas (1859) on the ratio between magnesium chloride and silver only showed the inapplicability of the method, for in spite of heating in a current of hydrochloric acid, it was found impossible to prepare magnesium chloride perfectly free from oxygen. Marignac has lately (1883) obtained results by means of the old method of analysis and synthesis of the sulphate which satisfy the requirements justly expected of a constant so frequently in use. He found $Mg = 24 \cdot 38$. The number even yet almost always employed, $Mg = 24 \cdot 00$, is thus over 1·5 per cent wrong.

A source of error has since been found in the work of Burton and Vorce (1890); there are good estimations by Richards and Parker (1896) based on the ratio $MgCl_2 : 2Ag$. Their results are in close agreement with those of Marignac, and the number $Mg = 24 \cdot 33$ may be considered correct to 1 unit in the last place.

39. *Manganese.*—The older values for the atomic weight of manganese were somewhat uncertain; Hauer (1857) was the first to give accurate numbers, which he obtained by converting manganese sulphate into sulphide by ignition in a current of sulphuretted hydrogen. This method is much better than that again used by Dumas, viz. the titration with silver, as the impossibility of obtaining pure chloride became once more apparent. A series of experiments by Schneider (1859), who subjected the oxalate to combustion, is also not quite faultless. Dewar and Scott (1883) analysed silver permanganate, $AgMnO_4$, and Marignac (1883) and Weeren (1890) converted manganous oxide into the corresponding sulphate; both methods gave results agreeing with each other and with those of Hauer. Very accurate experiments of Baxter and Hines (1906) gave $MnBr_2 : 2AgBr = 1 : 1 \cdot 74888$, $MnBr_2 : 2Ag = 1 : 1 \cdot 00463$, $MnCl_2 : 2AgCl = 1 : 1 \cdot 71447$, $MnCl_2 : 2Ag = 1 : 2 \cdot 27717$. This gives $Mn = 54 \cdot 96$.

40. *Mercury.*—There has never been much doubt as to the atomic weight of this metal, as even the oldest analyses of mercuric oxide by Sefström give a number very near the right one. Later determinations have been made by different methods. Turner (1833) analysed, besides mercuric oxide, mercuric and mercurous chlorides by ignition with lime, Erdmann and Marchand (1844) reduced mercuric oxide with charcoal and mercuric sulphide with metallic copper, Millon (1846) and Svanberg (1848) repeated the decomposition of mercuric chloride by heating with lime. Hardin (1896) used electrolytic methods. As mean of all the determinations we may take $Hg = 200 \cdot 0$.

41. *Molybdenum.*—The oldest experiments of Berzelius (1818) were on the conversion of lead nitrate into lead molybdate, and gave much more correct numbers than those of Svanberg and Struve (1848), who transformed the sulphide, MoS_2, into the oxide, MoO_3, by roasting. In this process there is a loss of weight of only some 10 per cent, so that the errors of experiment have a great influence on the result. Dumas (1859), on the other hand, obtained good numbers by reducing the strongly heated trioxide in a stream of hydrogen to the metallic state. The analysis of the chlorides of molybdenum by Liechti and Kämpe (1873) may also be used, and lately von der Pfordten (1884) has found the same value from the analysis of ammonium molybdate. Smith and Maas (1893) heated sodium molybdate in a current of hydrochloric acid, and weighed the residual sodium chloride. Seubert and Pollard dissolved the trioxide in sodium hydroxide, and estimated the equivalent by titration; they also reduced it by means of hydrogen to metal. The mean is Mo = 96·0. Van den Berghe (1898) oxidised the metal to trioxide by means of nitric acid and found Mo = 96·07, in close agreement with Seubert and Pollard.

42. *Neodymium, Praseodymium* (*Didymium*).—The same observations as were made on cerium (p. 131) apply also to this element. The old data of Marignac (1849 and 1853), Hermann (1861), Zschiesche (1869), and Erck (1870) all vary greatly. They were mostly obtained from the precipitation of didymium sulphate by barium chloride, and are affected with an error caused by the barium sulphate under these conditions taking down with it considerable quantities of didymium oxide by adsorption. However, experiments of Cleve, Nilson and Pettersson, and Brauner, who all converted the sulphate into the oxide by ignition, yielded discordant numbers in spite of the identical methods. In 1885 Auer von Welsbach reported that he had split the "element" hitherto known as didymium into two others, which he called praseodymium and neodymium. The atomic weights are, according to the preliminary experiments, which were not extended at the time, Pr = 143·6 and Nd = 140·8.

Welsbach's results were for long unchecked by other investigations. In recent times the work was resumed owing to the use of rare earths in the incandescent gas lamp industry. It then turned out that although the two constituents of didymium do exist, the atomic weights were exactly reversed. Researches by Scheele, Brauner and Jones (all in 1898) all led to the same result. Feit and Przibylla (1906) titrated the oxides with sulphuric acid, Holmberg (1907), Wild (1905), Brill (1905), Auer (1903), Brauner (1901) determined the same ratio, partly volumetrically, and partly by gravimetric analysis. The very concordant and reliable results of Brauner are Nd = 143·9, Pr = 141·0.

43. *Neon* is a gas with the same general properties as argon, and was discovered by Ramsay (1889). From the density, Ramsay and Travers obtained Ne = 19·94.

44. *Nickel.*—Almost all the chemists who attempted to fix the atomic weight of cobalt have at the same time extended their investigations to nickel and found here also very varying results—from 58·0 to 59·4. The discovery of the volatile nickel carbonyl, which has no cobalt analogue, has made it possible to obtain nickel preparations free from cobalt (1890), and in consequence the atomic weight has been determined with greater certainty. The best numbers are those of Richards and Cushman (1898 and 1902). From the analysis of nickel bromide, they found $NiBr_2 : 2AgBr = 1 : 1·71909$, and $NiBr_2 : 2Ag = 1·01268 : 1$; by heating the bromide in a current hydrogen $NiBr_2 : Ni = 1 : 0·26854$. Both give Ni = 58·60.

45. *Nitrogen.*—A great many different methods have been used for this element. Berzelius (1811) determined the ratio between ammonium chloride and silver chloride. He afterwards used the proposition that the specific gravities of the gaseous elements are proportional to their atomic weights (see below), and based the number considered by him as correct on weighings of oxygen and nitrogen which he executed in conjunction with Dulong (1820). Turner (1833) determined the ratio between silver nitrate and chloride, between barium nitrate and sulphate, as well as between lead nitrate and sulphate.

Penny (1839), who made his admirably exact determinations with the simplest imaginable apparatus, converted potassium chlorate into potassium nitrate by evaporation with nitric acid, and in the same way potassium chloride into nitrate, and conversely. He also deduced the atomic weight of nitrogen from the ratio between silver and its nitrate, as well as between the nitrate and chloride. His results agree almost absolutely with those of Stas, which were made much later.

In spite of their excellence, Penny's results remained almost neglected, and a much less correct value given by Berzelius was used until Dumas and Boussingault showed its inaccuracy from the comparative weights of oxygen and nitrogen. Berzelius then caused a new determination to be made by Svanberg (1842), who converted lead into lead nitrate, without, however, obtaining very exact results. Good numbers were obtained by Pelouze (1843), who titrated ammonium chloride with silver; by Marignac (1842), from the transformation of silver into silver nitrate; and by Regnault (1845), from his gas-density determinations. Dean (1899) determined the ratio KBr : AgCN, Scott (1901) with great accuracy that of ammonium chloride to silver, and ammonium bromide to silver. The very exact determination of silver and nitrate in silver nitrate by Richards and Forbes gave $Ag : NO_3 = 1 : 0·57479$. Recently the densities of nitrogen and of the oxides of nitrogen have been frequently determined. Guye (1900) found from pure nitrogen 14·004, Guye and Bogdan (1904) from nitrous oxide 14·007, Jaquerod and Bogdan (1904) by analysis of nitrous oxide 14·019. Gray (1905) from the density of nitric oxide got 14·006, from its combustion 14·016, and from the density of nitrogen 14·008. Density determinations by Leduc, Lord Rayleigh, Perman, etc., led to the same result (14·005 to 14·010). The densities are measured at finite pressures and the zero value found by extrapolation by means of van der Waal's law. The number now adopted N = 14·008 is based on the last named investigations and is preferable to Stas's number 14·04; it may even be too high by some units in the last place.

46. *Osmium.*—For this element, too, a single analysis of potassium osmium chloride by Berzelius (1828), which gave Os = 200, had to serve until quite recently. Seubert in 1888 made an exact determination by the analysis of ammonium and potassium osmium chlorides, and this led to a much smaller value which must be considered correct, viz. Os = 191.

47. *Oxygen.*—O = 16·000.

48. *Palladium.*—The case was the same for palladium as it was with osmium until 1889; our whole knowledge of its atomic weight is confined to two experiments by Berzelius in the year 1828, who analysed potassium palladium chloride.

In 1889 Keiser communicated the first results of his work, which he extended in 1894. Others were meantime engaged on the subject; Bailey and Lamb (1892), Keller and Smith (1892), Joly and Leidié (1893). Hardin (1899) reduced diphenylpalladiumdiammonium chloride and bromide, also ammonium palladium bromide to metal in a current of hydrogen, and found Pd = 107·0. Amberg (1905) estimated palladium in palladosammine chloride, both by precipitation with hydrazine sulphate and by electrolysis, and also estimated the chlorine. He found as a mean Pd = 106·5. The number adopted is Pd = 106·7.

49. *Phosphorus.*—For the determination of the atomic weight of this element many methods were tried by Berzelius without satisfactory results. Jacquelain's methods (1852), as well as his numbers, were still more diversified. Schrötter (1852) obtained trustworthy results, and these are still the best we know. He burned weighed quantities of red phosphorus (of which he was the discoverer) with oxygen to phosphorus pentoxide in a suitable apparatus. Similar experiments have been recently made by van der Plaats (1885), who obtained the same results.

Pelouze (1845) and Dumas (1859) applied the method of silver titration to the trichloride; here again the usual difficulty of obtaining pure chloride, in this case chloride free from oxychloride, was encountered. The numbers are therefore almost all too high.

Schrötter's experiments give P = 31·0.

50. *Platinum.*—The ill-luck which followed Berzelius in his determination of the atomic weight of the platinum metals—a want of success in striking contrast to the great trustworthiness of his other experiments—is found here in the case of platinum itself. The older data (1813 and 1826) which he obtained from the precipitation of a platinum solution by means of mercury and from the analysis of plantinous chloride were rejected by him in favour of a number, Pt = 197·2, based on the analysis of potassium platinic chloride (1828), although they were much nearer the truth. In 1881 Seubert showed a considerable error to exist in this determination, and from the analysis of potassium and ammonium platinic chlorides obtained the number Pt = 194·8. This number was soon afterwards confirmed by Halberstadt (1884). This atomic weight is important, for in the analysis of substances containing nitrogen this element is very often separated as ammonium platinic chloride and calculated from the residue of platinum left on heating. Up to 1881, therefore, the analyses made according to this method are affected with an error which makes the nitrogen appear less than it really is.

51. *Potassium.*—With exception of the very oldest experiments of Berzelius (1811), who converted metallic potassium (weighed as amalgam) into potassium chloride, the atomic weight of this metal has always been determined along with that of chlorine by the analysis of potassium chlorate. The different investigators who have taken part in this work are named on p. 131. The number in use till recently, K = 39·14 is due to Stas, and is very slightly changed. Richards and Archibald (1903), Archibald (1904), Richards and Stähler (1906), and Richards and Mueller (1907) determined the ratio KCl : AgCl, and KBr : AgBr, and also analysed potassium nitrate, and found K = 39·10.

52. *Praseodymium.*—See Neodymium.

53. *Radium.*—This element, discovered by the Curies (1898), has not been accurately investigated until quite recently. Mme. Curie (1902) found Ra = 225 from the analysis of the chloride. Repetition of the analysis with purer material (1907) gave 226·4. Thorpe (1908) found the same number.

54. *Rhodium.*—The number obtained by Berzelius (1828) from the analysis of sodium rhodium chloride appears to be somewhat more correct than those of the other platinum metals, for it has only been altered a unit by the new determinations of Jörgensen (1883), whose experiments, however, have only a preliminary character—according to them Rh = 103. Seubert and Kobbe (1890) found the same number.

55. *Rubidium.*—The new alkali metals rubidium and cæsium were discovered by Bunsen as the first-fruits of spectrum analysis. While the complete purification of cæsium did not succeed at once, rubidium

was very soon obtained free from admixed substances, and the number got from the analysis of the chloride (1861) has been confirmed by similar determinations due to Piccard (1862) and Godeffroy (1875). The mean is Rb = 85·4. Heycock (1882) analysed the chloride and the bromide, and obtained Rb = 84·36. Quite recently Archibald (1908) repeated both these analyses on carefully purified material and found Rb = 85·45.

56. *Ruthenium.*—The discoverer of this metal, Claus, to whose work we owe almost our whole knowledge of the element, determined its atomic weight by the analysis of potassium ruthenium chloride, K_2RuCl_5. The result was Ru = 103·8. Joly has lately (1889) found a considerably smaller value, viz. Ru = 101·7.

57. *Samarium.*—This element is still less certainly a single pure substance than the other metals of the rare earths. Cleve (1884), who converted the oxide into sulphate, gives the value Sm = 150. Later investigations show that the old samarium contained europium. The new number obtained by Urbain and Lacombe (1904) is Sa = 150·4.

58. *Scandium.*—This element also belongs to the "rare earths," but it is far more probably a pure substance than the others, from which it differs very decidedly by its small atomic weight. Nilson (1880), who discovered it simultaneously with Cleve, gives Sc = 44·1 from the conversion of the oxide into sulphate.

59. *Selenium.*—The determination of the atomic weight of selenium has been attended with considerable difficulty. Berzelius (1818) employed a quite unusual process—the conversion of weighed quantities of selenium into the tetrachloride, $SeCl_4$ — and placed more confidence in the number got in this way than in those from the analysis of silver selenide and barium selenite. A publication of Sacc (1847) contains merely a list of unsuccessful experiments. A short report of the analysis of mercury selenide is due to Erdmann and Marchand (1852). Dumas finally repeated (1859) the experiments of Berzelius on the formation of the tetrachloride.

The number at present in use is founded on an investigation by Ekman and Pettersson (1876), in which, on the one hand, selenium was converted into the dioxide, and on the other silver selenite transformed into silver chloride. The mean is Se = 79·1. Besides a not very accurate investigation of Steiner (1901), there are researches by Lenher (1898) and J. Meyer. The latter electrolysed silver selenite and weighed the silver. Lenher converted the same salt into silver chloride by means of a current of HCl, and reduced the silver chloride to metal by means of hydrogen; he also reduced the double ammonium bromide to selenium. The results of the two last-named authors give Se = 79·2.

60. *Silicon.*—The atomic weight of this element was known before the element itself. Berzelius (1810) and, with better success,

Stromeyer (1811) prepared iron rich in silicon, and oxidised weighed quantities of this. The product of oxidation was analysed, and after subtraction of the iron from the original substance and of the iron oxide from the product, the ratio of silicon to silicon dioxide was obtained. Berzelius afterwards investigated various silicates, both natural and artificial, as well as barium silicofluoride, without, however, obtaining satisfactory results.

The application of silver titration yielded accurate numbers. After the first experiments by Pelouze (1845), the process was applied by Dumas (1859) and Schiel (1861), with the same results. Thorpe and Young have lately (1887) decomposed weighed quantities of silicon tetrabromide with water and weighed the resulting silica. The result is Si = 28·4. This value may be too high. J. Meyer and Becker (1905) prepared very pure silicon tetrachloride, and turned it into dioxide. From the ratio $SiCl_4 : SiO_2 = 2{\cdot}82318 : 1$, Si = 28·24.

61. *Silver.*—The atomic weight of silver has always been determined simultaneously with those of chlorine and potassium, so that the data given on p. 125 may be referred to. The number at present accepted, and it must be considered the best known of all the atomic weights, was determined by Stas according to five independent methods, the results of which here follow :—

a. Analysis of potassium chlorate and determination of the ratio KCl : Ag	107·940
b. Analysis of silver chlorate and synthesis of silver chloride	107·941
c. Analysis of silver bromate and synthesis of silver bromide	107·923
d. Analysis of silver iodate and synthesis of silver iodide	107·937
e. Analysis of silver sulphate and synthesis of silver sulphide	107·927

The mean value is Ag = 107·938, and its probable error, calculated from the deviation from the mean value, is less than four units in the last place.

In spite of this exact agreement, the results of Stas are doubtful according to newer results, apparently because of systematic errors. A new basis must therefore be sought. The only recent result available is that of Richards and Forbes (1907) from the synthesis of silver nitrate. According to it, if O = 16·000 and N = 14·008, Ag = 107·883.

62. *Sodium.*—Berzelius (1811) determined the atomic weight of this metal, like that of potassium (p. 142), by conversion of the metal in sodium amalgam into sodium chloride. Penny (1839) found an almost absolutely correct value by the reduction of sodium

chlorate to chloride. Pelouze (1845), Dumas (1859), and Stas determined the ratio between sodium chloride and silver; the results of the last give the number Na = 23·06. From the investigation of Richards and Wells (see chlorine) this result appears to be erroneous, and the most accurate value is Na = 23·00.

63. *Strontium.*—We are indebted for our first knowledge of the atomic weight of this element to Stromeyer (1816), who analysed the carbonate and chloride. Pelouze (1845), Marignac (1858), and Dumas (1859) titrated strontium chloride with silver and obtained concordant results. Richards estimated (1894) the ratio between strontium bromide and silver bromide or silver, also (1905) of the chloride to silver, and obtained what must be regarded as the correct value, Sr = 87·63.

64. *Sulphur.*—The process by means of which Berzelius (1811) ascertained the atomic weight of sulphur for the first time, consisted in combining the same weight of lead first with oxygen, and then with sulphur; the number obtained was, to be sure, not very exact. He afterwards (1818) converted lead into lead sulphate, an experiment which Turner repeated (1833). Erdmann and Marchand (1844) analysed mercuric sulphide after fixing the atomic weight of mercury by analysis of the oxide (p. 138). Berzelius, who doubted their results, converted (1845) silver chloride into sulphide by heating in hydrogen sulphide. Struve (1851) decomposed silver sulphate by heating it in a current of hydrogen, when pure silver remains, and lastly, Dumas (1859) converted silver into silver sulphide by heating it in sulphur vapour.

The results of the majority of the experiments give values lying close to S = 32·0. It follows, however, from the more exact determinations of Stas, that the true value is somewhat greater. Richards (1891) determined the ratio $Na_2CO_3 : Na_2SO_4$, but does not consider it very accurate. On the other hand, Richards and Jones (1907) determined the ratio of silver sulphate to silver chloride with great exactness. From it for Ag = 107·88, S = 32·06.

65. *Tantalum.*—The atomic weight of this rare element is not even yet known with certainty. The older experiments of Rose, Berzelius, and Hermann gave quite untrustworthy results. The best numbers are got from the conversion of potassium tantalum fluoride into tantalic acid and potassium sulphate, by Marignac. Hinrichsen and Sahlbom (1906) oxidised tantalum to pentoxide. The result is probably preferable to Marignac's number (182). It gives Ta = 180.

66. *Tellurium.*—Berzelius (1812 and 1833) oxidised tellurium to dioxide. His numbers were closely confirmed by those of Hauer (1857), who analysed potassium tellurium bromide. Wills (1879) repeated both experiments and got the same results.

In spite of this agreement the number obtained, Te = 128, must be considered improbable. For if we compare the following rows

P = 31·0 As = 75·0 Sb = 120·4
S = 32·1 Se = 79·1 Te = 128
Cl = 35·46 Br = 79·91 I = 126·93

we find in the three groups P, As, Sb; S, Se, Te; and Cl, Br, I, each of which comprises three similar elements, sulphur between phosphorus and chlorine, and selenium between arsenic and bromine; but tellurium with the number 128 does not stand between antimony and iodine. Brauner (1883) found a source of error in the older determinations and obtained from the oxidation of tellurium to dioxide and from the formation of the sulphate $Te_2O_4SO_3$ the atomic weight Te = 125, corresponding to analogy. This result, however, is by no means confirmed by later work. Gooch and Howland (1894) oxidised an alkaline solution of the dioxide with permanganate, and obtained Te = 127·0; Staudenmayer reduced crystallised telluric acid to dioxide and found 127·2 to 127·6. Chikashig (1896) decomposed tellurium bromide by heating with silver, and found 127·6. Köthner (1902) analysed the basic nitrate $Te_2NO_3O_4H$, Gutbier (1902 and 1905) determined the water and tellurium in telluric acid H_2TeO_4, $2H_2O$, and also reduced tellurous acid to tellurium. This reduction and its converse were done by Pellini (1901) and Heberlein (1898). Norris (1907) repeated Köthner's work. Leaving out of account as not very accurate an analysis of diphenyltelluride by Steiner (1901), all these experiments lead to Te = 127·6. The atomic weight of tellurium must, therefore, be regarded as higher than that of iodine.

It remains to be seen whether the result of Marckwald (1907), who found Te = 126·9 from the estimation of water in telluric acid, will be confirmed.

67. *Terbium.*—This element, like most of the metals of the rare earths, is not yet certainly known to be a single substance. It was discovered by Mosander (1842), and its atomic weight differs with its purity. The most recent result of Urbain (1905) obtained from the amount of water in the hydrated sulphate is Tb = 159·2.

68. *Thallium.*—The first determinations by one of the two discoverers of thallium, Lamy (1862), from the analysis of the chloride and sulphate are not very exact. The results obtained by Werther (1864) from the analysis of thallium iodide and by Hebberling (1865) from the repetition of Lamy's experiments are but little better. A research executed by the other discoverer, W. Crookes (1873), with all imaginable precautions, but unfortunately only according to one method (the conversion of the metal into the nitrate), gave Tl = 204·0. A new investigation by

Lepierre (1894), employing three different methods, fully confirmed the number found by Crookes, which may therefore be retained, although a determination of the ratio of thallous chloride to silver chloride by Wells and Penfield (1894) gave the very divergent value 204·5.

69. *Thorium.*—Berzelius, who discovered this element, determined its atomic weight (1829) by analysis of the sulphate. The experiments were subsequently repeated by Chydenius (1863), Delafontaine (1863), Hermann (1864), and Cleve (1874), the analysis being mostly so conducted that thoria remained behind on strong ignition of the salt. Cleve analysed the oxalate in addition. Nilson, at first alone (1882), afterwards in conjunction with Krüss (1887), performed the analysis of the sulphate with material purified with special care. Both researches yield the same number, Th = 232·4, which is somewhat lower than that found by the older investigators. Lately, Brauner (1901) and Baskerville (1901) stated that thorium could be split up into other elements; this would be in accordance with the transformations of radioactive substances observed by Rutherford and others. R. J. Meyer and Gumperz (1905), however, were unable to confirm this. Their analysis of thorium sulphate octohydrate gave Th = 232·5.

70. *Thulium.*—A very doubtful element, to which Cleve (1880) gives the atomic weight Tu = 171 from analysis of the sulphate.

71. *Tin.*—The oxidation of the metal to dioxide has been almost exclusively employed for the determination of this atomic weight. We have such experiments by Berzelius (1812), Mulder and Vlandeeren (1849), Vlandeeren (1858), Dumas (1858), and van der Plaats (1885). In agreement with them are two analyses of the tetrachloride by Dumas. The mean value is Sn = 118·1. Bongartz and Classen (1888) have found with different methods a number higher than this. The older results do not seem to be absolutely displaced by this, but provisionally we may put Sn = 119·0.

72. *Titanium.*—The oldest determinations are due to H. Rose (1823 and 1829), and were obtained by roasting titanium sulphide to dioxide, and from the analysis of titanium chloride. The latter method has again been employed by Pierre (1847), Demoly (1849), and lastly by Thorpe (1883 and 1885), whose exact researches, which were also extended to titanium bromide, give Ti = 48·1.

73. *Tungsten.*—The atomic weight of tungsten has been usually determined from the reduction of the trioxide to metal, and from the oxidation of the metal to trioxide,—Berzelius (1825), Schneider (1850), Borch and Dumas (1859). Roscoe (1872) from an analysis of the hexachloride obtained the same result. Other determinations, such as the analysis of barium metatungstate by Scheibler (1861) and of ferrous tungstate by Zettnoff (1867),

are of less importance. Later researches by Waddell (1886), Pennington and Smith (1894) on the reduction of the trioxide, gave results which did not agree. More recently, experiments by Thomas (1899), Hardin (1897 and 1899) and Taylor (1901) gave from the oxidation of tungsten to the trioxide, a mean value of 184·0, from the reverse reaction the smaller figure 183·7. The cause of the discrepancy is probably the volatility of the oxide, so that the oxidation does not give good results. Further, the metal occludes a little hydrogen. The most trustworthy results are those of Smith and Exner (1904) from the conversion of the hexachloride into oxide, and, with special precautions, of the metal into oxide. Both series gave concordant results: W = 184·0.

74. *Uranium.*—Up to the year 1840 the atomic weight of uranium had been calculated quite erroneously from the experiments of Arfvedson (1825) and Berzelius (1825), for the black product UO_2 got by the reduction of the higher oxides was looked upon as metallic uranium until Péligot showed that it contained oxygen. He at the same time determined the atomic weight pretty accurately from analysis of uranyl acetate. Later researches by Ebelmen (1842) and Wertheim (1843) are of little importance, but the very careful work of Cl. Zimmermann (1882 and 1886) deserves attention. The methods employed were not in themselves particularly good, but excellent results were obtained by scrupulous care being used in the performance of the experiments. One series consisted in the reduction of U_3O_8 to UO_2 in a current of hydrogen, the other in the conversion of sodium uranyl acetate, $Na(UO_2)(C_2H_3O_2)_3$, into sodium diuranate, $Na_2U_2O_7$, by roasting. Aloy (1901) determined the ratio between uranium and nitrogen in the nitrate. The most accurate results were obtained by Richards and Merigold (1902) by transforming uranium tetrabromide into silver bromide: from them U = 238·0. It may be mentioned that uranium has the highest atomic weight of all the elements.

75. *Vanadium.*—An error similar to that in the case of uranium was also committed with this metal. It was only found out in 1868 by Roscoe, who showed that the substance formerly held to be the metal was really an oxide VO. If we take this into account in calculating the analyses of vanadic acid and of vanadyl chloride by Berzelius (1831), we arrive at pretty correct numbers. Our present accurate knowledge of the atomic weight of this element is due to an excessively careful investigation by Roscoe (1868), who reduced vanadic acid to oxide in a current of hydrogen, and also titrated vanadyl chloride with silver. The mean of the two series is V = 51·2.

76. *Xenon.*—This is another element of the type of argon, and was discovered by Ramsay and Travers (1898). The density as found by its discoverers, gives X = 128·0.

77. *Ytterbium.*—Marignac in 1872 discovered in the substance regarded up till that time as erbia a perfectly colourless earth with no absorption spectrum, to which he gave the name of ytterbia. Immediately thereafter, Delafontaine found the same substance in allanite from Amherst, and Nilson, too, soon confirmed the existence of the new element. Its atomic weight was found by these three authors and also by Brauner pretty concordantly to be Yb = 173·0. It has since been resolved by Auer von Welsbach (1907) into two different earths, whose elements have been named (Neo)ytterbium and Lutecium, with the atomic weights Yb = 172·9 and Lu = 174·2.

78. *Yttrium.*—This element also was only gradually distinguished and separated from the earths which always accompany it, and we cannot even yet state with certainty that what is known as yttrium is really a chemical species. Delafontaine (1865) was probably the first to work with tolerably pure material. The method he adopted was the conversion of the earth into sulphate, and this was also done by Bahr and Bunsen (1866), Cleve and Höglund (1873), and Cleve (1873), Marignac (1880), Jones (1895). G. and E. Urbain found 88·6; Feit and Przibylla (1906) by titration of the oxide with sulphuric acid, 89·4. The mean of all the results is very nearly Y = 89·0.

79. *Zinc.*—Even the oldest researches by Gay-Lussac (1809), and Berzelius (1811) yielded a result very near the truth. The method was the conversion of the metal into oxide. The number obtained was called in question on quite insufficient grounds by Jacquelain in 1842, and shortly thereafter Favre sought by the analysis of zinc oxalate, as well as by dissolving zinc in sulphuric acid and burning the evolved hydrogen to water, to show the correctness of a higher value. Berzelius caused A. Erdmann (1843) to undertake new oxidation experiments, which approximately confirmed his previous numbers. Still nearer Berzelius's value are the numbers lately found by Marignac from the analysis of potassium zinc chloride. Baubigny (1883) by analysis of the sulphate, Gay-Lussac (1809), van der Plaats (1885), and Mallet (1890) by solution of zinc in sulphuric acid and measurement of the hydrogen evolved, and lastly Ramsay and Reynolds (1887) by the same methods have found similar values. Morse and Burton determined the ratio Zn : ZnO, but overlooked the fact that oxides obtained by heating nitrates retain oxygen and nitrogen even after strong ignition. Gladstone and Hibbert (1889) determined the atomic weight by an electrolytic method. Finally, Richards and Rogers (1895) determined the ratio between zinc bromide and silver. These give the most reliable result: Zn = 65·40. The result of Morse and Burton is almost identical if a correction is applied for the occlusion (Morse and Arbuckle, 1898).

80. *Zirconium.*—The atomic weight of this element has not been often determined: once by Berzelius (1825) from the analysis of

the sulphate, and once by Marignac (1860) from the analysis of potassium zirconium fluoride. The latter obtained Zr = 90·7. Weibull (1881) and Bailey (1889) repeated the experiments of Berzelius. The latter's results gave Zr = 90·6 in close agreement with Marignac's number.

In the following table the atomic weights of the elements at present known are collected; O = 16·000 is taken as the basis of the calculation.

Aluminium	Al	27·1
Antimony	Sb	120·2
Argon	A	39·9
Arsenic	As	74·96
Barium	Ba	137·37
Bismuth	Bi	208·0
Boron	B	11·0
Bromine	Br	79·92
Cadmium	Cd	112·40
Cæsium	Cs	132·81
Calcium	Ca	40·09
Carbon	C	12·00
Cerium	Ce	140·25
Chlorine	Cl	35·46
Chromium	Cr	52·0
Cobalt	Co	58·97
Columbium (Niobium)	Cb	93·5
Copper	Cu	63·57
Dysprosium	Dy	162·5
Erbium	Er	167·4
Europium	Eu	152·0
Fluorine	F	19·0
Gadolinium	Gd	157·3
Gallium	Ga	69·9
Germanium	Ge	72·5
Glucinum	Gl	9·1
Gold	Au	197·2
Helium	He	4·0
Hydrogen	H	1·008
Indium	In	114·8
Iodine	I	126·92
Iridium	Ir	193·1
Iron	Fe	55·85
Krypton	Kr	83·0
Lanthanum	La	139·0
Lead	Pb	207·10
Lithium	Li	7·00
Lutecium	Lu	174·0
Magnesium	Mg	24·32
Manganese	Mn	54·93
Mercury	Hg	200·0
Molybdenum	Mo	96·0
Neodymium	Nd	144·3
Neon	Ne	20·0
Nickel	Ni	58·68
Nitrogen	N	14·01
Osmium	Os	190·9
Oxygen	O	16·00
Palladium	Pd	106·7
Phosphorus	P	31·0
Platinum	Pt	195·0
Potassium	K	39·10
Praseodymium	Pr	140·6
Radium	Ra	226·4
Rhodium	Rh	102·9
Rubidium	Rb	85·45
Ruthenium	Ru	101·7
Samarium	Sa	150·4
Scandium	Sc	44·1
Selenium	Se	79·2
Silicon	Si	28·3
Silver	Ag	107·88
Sodium	Na	23·00
Strontium	Sr	87·62
Sulphur	S	32·07
Tantalum	Ta	181·0
Tellurium	Te	127·5
Terbium	Tb	159·2
Thallium	Tl	204·0
Thorium	Th	232·42
Thulium	Tu	168·5
Tin	Sn	119·0
Titanium	Ti	48·1
Tungsten	W	184·0
Uranium	U	238·5
Vanadium	V	51·2
Xenon	Xe	130·7
Ytterbium (Neoytterbium)	Yb	172·0
Yttrium	Y	89·0
Zinc	Zn	65·37
Zirconium	Zr	90·6

Numerical Relations of the Combining Weights.—Two directions have been taken in the attempts to draw general conclusions from the material offered by the atomic weights of the elements. A line of thought first pursued by Prout (1815) and shortly afterwards by Meinecke (1817) starts from the philosophical assumption of a fundamental substance or "protyle." This was thought to exist in hydrogen, and therefore the conclusion had to be drawn that, if all the other elements consisted of hydrogen, their atomic weights must be multiples of that of hydrogen.

This hypothesis was widely diffused in England, especially through the instrumentality of Thomas Thomson, the author of a then popular treatise on chemistry, who sought to support it by experiments, which were, however, very insufficient for the purpose. On the Continent it met with no success, Berzelius had declared it to be incorrect from the consideration of his own determinations; and the review of the whole question by Turner at the instigation of the British Association proved the accuracy of Berzelius's numbers.

However, when the error in the atomic weight of carbon was discovered in 1841, and this was shown by the work of Dumas and Stas to be to that of hydrogen as nearly as possible in the ratio 12 : 1, and when, in addition, Dumas found the atomic weights of oxygen and nitrogen to be respectively sixteen and fourteen times that of hydrogen, the French savant did not hesitate to express his conviction that a general law was here in question. He devoted himself afterwards to test this, and came to the conclusion that though all the atomic weights were not multiples of that of hydrogen, still the half of this value was the basis of all the others. He was afterwards forced, however, to halve this unit also, so that according to his latest views all the atomic weights might be represented as multiples of the fourth part of that of hydrogen.

The whole subject loses the greater part of its interest by this qualification, as the degree of accuracy of the determinations in the case of many elements does not reach the unit given by Dumas, so that the hypothesis cannot really be tested.

The same question was taken up simultaneously by J. S. Stas, who restricted himself to the investigation of fewer elements than Dumas, but far surpassed his teacher and former collaborator in the exactness of his determinations. Stas gives as the result of his researches the opinion that Prout's hypothesis is altogether inadmissible; it represents merely an approximation to the truth, all the atomic weights determined by him differing from those required by the hypothesis by quantities much larger than the possible errors of experiment can account for.

Although the question seemed finally settled by this work, it has nevertheless always sprung up again. The reason of this is the real approximation, already mentioned, of the values to multiples of the atomic weight of hydrogen. A glance at the table on p. 150 shows this plainly. There have consequently always been people who considered the integral values to be the only correct ones. No explanation at all probable of the actual deviations has yet been given; especially so as no chemical process is known in which the mass of the given material undergoes any change. We must therefore at present simply take the numbers as experiment gives them, and leave unanswered the question as to the cause of their surprising approximation to multiples of hydrogen.

Besides these considerations, hitherto fruitless, another series on the same subject but in a different direction has been pursued from the beginning. This series, in contrast to the former, has yielded well-defined regularities, which are submitted to the reader in the following pages.

Precursors of the Periodic Law.—J. B. Richter (1798), after his first discoveries on the mass relations exhibited when an acid is neutralised by different bases—the beginning of the scientific investigation of the subject,—at once conceived the idea that his constants, quite apart from their general significance, were subject to special laws. If they were arranged according to their magnitude, the numbers in his opinion followed a strict law, for which he assumed different expressions at different times. The general acceptance of the fundamental law discovered by Richter was much retarded by his holding to the above idea with such tenacity that he almost lost sight of the chief discovery. However, he was so far justified in that the regularities suspected by him actually exist, although not in the form he attributed to them.

At first only the constant combining numbers for acids and bases, and afterwards those for metals, received the above-mentioned generalisation, a generalisation which led to the atomic theory. Soon after the advancement of this theory, Döbereiner (1817) drew attention to a certain regularity by showing that the atomic weight of strontium (87·6) lay midway between the atomic weight of calcium (40·1) and that of barium (137·4). For our more exact numbers, which I have placed in brackets, this is not strictly true, as the calculated value is 88·7 instead of 87·6, but the approximation is at all events remarkable, especially as we find the same thing repeated several times. Lenssen (1857), indeed, attempted to arrange all the elements in triads in this way.

Pettenkofer's supposition (1850), that the atomic weights of similar elements form arithmetical series, is more like the original ideas of Richter again. Kremers, Gladstone, and especially Dumas, further developed the subject in various ways.

The Periodic Law.—The idea which proved to be the most fruitful was advanced by Newlands in 1864, although in somewhat inadequate form, so that it did not find ready recognition. He not only arranged the similar elements in series, but also the whole of the elements according to the magnitude of their atomic weights. It appeared from this arrangement that similar elements were found at approximately equal distances in the series; counting from any one element, every eighth was in general more similar to the first than the other elements. This he called the Law of Octaves, but did not succeed in fully carrying it out.

Lothar Meyer and Mendelejeff independently (1869) met with more success, and their conclusion may be expressed as follows: the properties of the elements are periodic functions of their atomic weights. Thus, if all the elements are arranged in the order of their atomic weights in a series, their properties will so vary from member to member that after a definite number of elements have been passed either the first or very similar properties will recur.

The carrying through of this idea met with great difficulties at the outset. The reason lay partly in the fact that at that time there was no systematic way of choosing the true atomic weight from those that appeared probable. For instance, if it is determined that carbon combines with oxygen in the ratios 12 : 16 and 12 : 32, it is, without other information, quite arbitrary to assume in the first compound one atom of carbon to one atom of oxygen, and in the second, one atom of carbon to two atoms of oxygen. We might just as well put the atomic weight of carbon equal to 6 and write the compounds C_2O and CO, or equal to 24, when the formulæ would become CO_2 and CO_4. The sides from which this problem of the right choice of the atomic weights could be attacked were manifold, as will be seen later, but at the period when Meyer and Mendelejeff developed their views there was no agreement as to how the attack ought to be made, although the general principles had been to a great extent discovered. In fact the principle we are discussing had often to be applied to decide between the possible values.

Besides this difficulty another had to be overcome, namely, that which lay in the actual false determination of some equivalents. Here, however, it was generally merely a question of transposing two neighbouring elements, several instances of which have been already mentioned, a more correct determination being brought about by this circumstance. Mendelejeff was both most energetic and most successful in this respect.

The annexed table of the elements arranged according to their atomic weights is practically that of L. Meyer, extended to include the newly discovered elements. The series is divided into eight classes, so arranged that the individual members of the first, third, fifth, seventh, ninth and eleventh rows are more nearly related to each other than to the even rows, and similarly with the even rows.

0	I	II	III	IV	V	VI	VII	
He 4	Li 7	Gl 9·1	B 11	C 12	N 14	O 16	F 19	—
Ne 20	Na 23	Mg 24·4	Al 27·1	Si 28·2	P 31·0	S 32·1	Cl 35·5	—
A 40	K 39·1	Ca 40	Sc 44·1	Ti 48·1	V 51·2	Cr 52·1	Mn 55·0	Fe 56, Ni 58·7, Co 59
Kr 81	Cu 63·6	Zn 65·4	Ga 70	Ge 72	As 75	Se 79·1	Br 80·0	—
X 128	Rb 85·4	Sr 87·6	Y 89	Zr 90·6	Cb 94	Mo 96·0	—	Ru 102, Rh 103, Pd 106
—	Ag 107·9	Cd 112	In 114	Sn 118·5	Sb 120	Te 127·6	I 126·9	—
—	Cs 133	Ba 137·4	La 138, etc.	—	—	—	—	—
—	—	—	—	—	—	—	—	—
—	—	—	Yb 173	—	Ta 183	W 184	—	Os 191, Ir 193, Pt 195
—	Au 197·2	Hg 200·3	Tl 204·1	Pb 206·9	Bi 208	—	—	—
—	—	—	—	Th 232	—	U 238	—	—

The similar elements are thus found in the same column, the likeness in many cases (but not always) being previously recognised in the attempt to form "natural" families of elements. The members of the even rows and of the odd rows consist of the elements which are most closely related; the affinity between the odd and even columns is not so great.

The analogies are most marked in the general chemical properties, especially in the capability of forming acids or bases. Taking the table, we have in the first double column the quite indifferent gases of the argon type; then follow the very strongly basic alkali metals, and the likewise strongly basic metals of the alkaline earths in the third column; then follow the metals of the earths whose oxides are weakly basic; next come the elements of the carbon group, the oxides of which are partly weak acids, the acid properties in each column diminishing with increasing atomic weight. The members of the seventh column are already decidedly acid-forming, and those of the eighth exhibit this property in the most marked manner.

A very remarkable regularity is observed with respect to the valency of the elements, as is indicated by the Roman numerals in the table. This property increases from 1 to 4; from this point on the elements have mostly more than one valency, one towards chlorine, oxygen, etc., which increases as we proceed, and one towards hydrogen, which decreases at the same rate.

Further regularities shown by the physical properties of the elements as well as of their compounds in the preceding arrangement will be discussed later.

Discussion.—In both tables there are many vacant places. They belong to elements not yet discovered. Mendelejeff made use of the regularities just mentioned to predict the properties of unknown elements from those of their neighbours in the table. He gave especially a somewhat detailed description of scandium, gallium, germanium, and their compounds, none of which were known at the time he wrote his memoir, and to him as well as to science in general has been accorded the triumph of seeing these predictions for the most part fulfilled on the subsequent discovery of the elements.

To the extreme right of the table, and to some extent out of it, are the iron metals and the platinum metals. They show certain regularities, falling into three groups of three each with atomic weights very close together; in the platinum metals the elements also are exactly alike in the formulæ of the compounds which they can form. The elements of the argon type in the first column do not fit in well with the other elements, but form a group apart, with much less affinity to the succeeding column than is the rule.

The position of tellurium deserves attention. As previously stated, its atomic weight has been found to be greater than would be expected from its position in the periodic system, and repetition of the determinations has only seemed to confirm this (p. 146). As no one could think of changing the places of tellurium and iodine, there is a real contradiction between the arrangements according to atomic weight and according to natural affinity.

A similar case of inversion is repeated in Argon and Potassium.

Some explanation of this may be found in the fact that the differences of atomic weight between corresponding members in the table are not constant, but vary irregularly within fairly wide limits. If it were a rigid law, the atomic weights should not only decide the order in the series, but should be numerically arranged in a regular manner. We may therefore conclude that the relations expressed in the periodic system are the outcome of several independent factors whose influence varies.

The same circumstances which make these differences smaller or greater may, in some cases, bring about a change of sign, *i.e.* change the order of two elements in the series. This is what may occur in the case of iodine and tellurium; and the necessity of placing argon between chlorine and potassium points to a similar inversion of the sign of the difference.

After the symbol of lanthanum in the third series, "etc.," is added, to signify that the other "rare earths" cerium, neodymium and praseodymium are to be inserted here.

As there is only one place available here in the table, there is again an irregularity in the system. These elements are still more alike than the elements of the iron group, and thus it appears as if the circumstances which usually give rise to a single element, had here resulted in a number of very similar elements, somewhat after the fashion of the formation of asteroid planets.

The "periodic system" of the elements is by no means perfect. Elements are frequently parted in the preceding tables, which an unprejudiced observer would consider analogous in their compounds (*e.g.* copper and mercury), while others are placed together which appear altogether dissimilar, as sodium with copper, silver, and gold. It is to be hoped that such incongruities will be removed in the future by new facts and by fresh considerations. The periodic system is therefore not to be looked upon as the conclusion, but rather as the commencement of a train of ideas eminently fruitful.

We may conclude with an observation of a general character. From the fact that the mass of the various substances is not changed in a chemical process, it is apparent that the mass of a chemical compound is the sum of the masses of its components. Such properties, which are independent of the state of chemical combination, and whose numerical value in compounds therefore appears as the sum of the values belonging to the different components, will in future be called additive. From the existence of such properties it has been concluded that chemical compounds actually contain their components as such, the arrangement only being changed; the additive properties form, therefore, the foundation of the atomic theory; they are, however, independent of any hypothesis.

CHAPTER VII

GAY-LUSSAC'S LAW

In the course of experiments on the proportions by volume in which oxygen and hydrogen combine to form water, it was found at the end of last century that the ratio was 1 : 2. That they combined exactly in this proportion, as nearly as the experimental resources of that age allowed it to be determined, was first enounced by Gay-Lussac and Humboldt in 1805. Three years later Gay-Lussac established in a memoir, afterwards famous, that this was only a special case of a law that held for all gases. The law runs thus: If gaseous substances enter into chemical combination, their volumes are in simple rational proportions, and if a gaseous substance is formed by their union, its volume also is rationally related to the volume of the original gases. All the volumes must, of course, be measured at the same temperature and pressure.

This law evidently allows us to calculate the densities of gaseous compounds from those of their elements, if we know the volume relations on their formation. Two vols. hydrogen and 1 vol. oxygen give 2 vols. aqueous vapour. Now the specific gravity of hydrogen in the units given on p. 42 is 2·02, and of oxygen 32·00. We calculate now as follows:—

2 vols. hydrogen weigh 2 × 2·02 =	4·04
1 vol. oxygen weighs	32·00
The resulting 2 vols. aqueous vapour weigh	36·04
Consequently 1 vol. ,, ,, weighs	18·02.

Observation gives 18·05, an almost identical number.

If we consider that gases combine by weight in the proportion of their atomic masses or multiples of them, and now also in equal or multiple volumes, then we see that the weights of equal volumes of gases, or their specific gravities, must be to each other as their atomic weights or multiples of their atomic weights.

The idea is not far to seek, to so choose the atomic weights that their rational factors will agree with those of the volumes in chemical combinations. Then the weights of equal volumes of the various gases will be to each other as the atomic weights.

However, one difficulty militates so strongly against this simple assumption that we have no option but to let it drop. When chlorine and hydrogen unite to form hydrochloric acid gas, the volume remains unchanged, *i.e.* one litre of chlorine and one litre of hydrogen give two litres of hydrochloric acid. If we take such volumes of the two gaseous elements that each contains an atomic weight, there would be in the two volumes of hydrochloric acid only one combining weight, *i.e.* in the same volume only half a combining weight.

A similar difficulty presents itself in the case of water. Two volumes of hydrogen and one volume of oxygen unite to form two volumes of water vapour. In the above sense this would mean that one combining weight of oxygen unites with two combining weights of hydrogen to form water; since this has double the volume of the oxygen, there would be in a single volume only half a combining weight of water, again in contradiction to the general law as to the combining weights of compound substances.

The case of phosphine is still worse. One vol. of phosphorus vapour unites with 6 vols. of hydrogen, and 4 vols. of phosphine result. The combining weight of phosphine would be only one-fourth of the sum of its constituents.

We are driven to the conclusion that a simple proportionality between gas density and combining weight is out of the question, unless we are willing to admit fractions of combining weights, which, from a purely stoichiometric point of view (p. 116) as well as that of the atomic hypothesis, is not permissible. A factor must be introduced, which will differ from case to case, and the law of Gay-Lussac indicates only that these factors must be rational numbers.

Molar Weights.—The problem now before us is to fix the smallest whole numbers which will permit of a consistent representation of the relations. Using the name molar weight for the density referred to the normal gas (p. 42), we have the question: how many combining weights are there in the molar weight, so that the molar weight of the compound shall at least be equal to the sum of the combining weights of the elements?

In the case of hydrochloric acid, the assumption suffices that a molar weight of chlorine and hydrogen each contains two combining weights, and that molar weight and combining weight are the same in hydrochloric acid. A similar assumption serves for water. But for phosphine, it must be assumed that phosphorus vapour contains four combining weights in the molar weight, in order that there shall be one combining weight of phosphorus in each of the 4 vols. of phosphine. In general, if one volume of a constituent results in n volumes of the compound, there are n combining weights in one molar weight of that constituent.

If the chemical formulæ are written in such a way that they represent molar weights, or that the quantities expressed by the formulæ are proportional to the gas densities, the above-mentioned ratios are shown very distinctly. We have the equations:—

$$H_2 + Cl_2 = 2HCl.$$
$$2H_2 + O_2 = 2H_2O.$$
$$P_4 + 6H_2 = 4PH_3.$$

Considered in the light of these equations, all chemical reactions in which substances participate which are known in the form of gas or vapour, go to show that for oxygen, nitrogen, hydrogen, chlorine, bromine and iodine, two combining weights are contained in one molar weight; no compound is known a molar weight of which contains less than half a molar weight of these elements. This is the reason for referring molar weights to a unit which makes the molar weight of oxygen 32, *i.e.* twice the combining weight.

For the few metallic elements which are known in the state of gas or vapour, the molar and combining weights are assumed to be identical. Phosphorus and arsenic require to have four combining weights in a molar weight. Sulphur and selenium are like the other non-metallic elements, but show abnormalities which require further mention.

The following table shows these relations clearly.

	Atomic Weight.	Molar Weight.	Ratio.
1. Oxygen . . .	16	32	2·00
2. Hydrogen . . .	1·01	2·02	2·00
3. Nitrogen . . .	14·01	28·01	2·00
4. Chlorine . . .	35·46	70·9	2·00
5. Bromine . . .	79·91	159·8	2·00
6. Iodine . . .	126·93	253·0	1·99
7. Sulphur . . .	32·06	65	2·03
8. Selenium . . .	79·2	160	2·02
9. Tellurium . . .	127·6	254	1·99
10. Phosphorus . .	31·0	129	4·16
11. Arsenic . . .	75·0	304	4·05
12. Mercury . . .	200	202	1·01
13. Cadmium . . .	112	114	1·02
14. Zinc	65·4	68	1·04
15. Potassium . . .	39·1	37·7	·96
16. Sodium . . .	23·0	25·5	1·11

This table is a confirmation of Gay-Lussac's law, that gas density and atomic weight are in simple ratios. The deviations from whole numbers are caused by the vapours and gases not exactly obeying the simple gas laws. In the latter part of the list the deviations are partly due to the very great experimental difficulties.

Compounds.—While the substitution of molar or molecular weights does not mark any advance in the case of elementary substances, the advantage becomes apparent in compounds. It is found that the combining or formula weight is the same as the molar weight. This is well seen in the following table:—

	Combining Weight.	Molar Weight Observed.
Water, H_2O	18·02	18·05
Ammonia, NH_3	17·04	17·10
Nitrogen monoxide, N_2O	44·08	44·25
Hydrochloric acid, HCl	36·47	36·52
Chlorine peroxide, ClO_2	67·5	68·68
Nitrosyl chloride, $NOCl$	65·5	67·53
Hydriodic acid, HI	127·9	128·6
Hydrogen sulphide, H_2S	34·0	34·48
Sulphur dioxide, SO_2	64·0	65·21
Sulphur monochloride, S_2Cl_2	134·9	136·2
Hydrogen selenide, H_2Se	81·1	81·16
Hydrogen Phosphide, H_3P	34·0	33·90
Phosphorus trichloride, PCl_3	137·4	141·5
Phosphorus oxychloride, $POCl_3$	153·4	154·5
Phosphorus sulphochloride, $PSCl_3$	169·4	171·0
Phosphorus pentasulphide, P_2S_5	222·3	222·3
Hydrogen arsenide, H_3As	78·0	78·25
Arsenic trioxide, As_4O_6	396·0	399·4
Arsenic trichloride, $AsCl_3$	181·4	182·6
Mercuric chloride, $HgCl_2$	271·2	284·0
Mercuric bromide, $HgBr_2$	360·2	352·4
Mercuric iodide, HgI_2	454·0	452·1
Cadmium bromide, $CdBr_2$	272·0	276·6

The two columns agree within the limits of experimental error, and the formula contains the smallest number of combining weights compatible with the given composition.[1] This has been attained by choosing the combining weights in the manner explained above and expressed in the previous table. The relation to gas density has led to a choice of combining weights which permits of a very simple and convenient representation of all the circumstances.

Compounds of Non-Volatile Elements.—These considerations may be still further extended. Obviously the validity of Gay-Lussac's law cannot depend on our experimental ability to investigate the vapour densities of all the elements. Now there are many compounds which are volatile, whose vapour density and molar weight are therefore known, although they contain non-volatile elements. The law must apply in their case also, in the general form that the molar weights of volatile compounds stand in a simple ratio to their combining weights.

It has proved feasible to choose all the combining weights of the elements in such a manner that on the one hand the quantities of

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[1] The only exceptions are arsenic trioxide and sulphur monochloride.

compounds represented by their molar weights are identical with their combining weights, and on the other these combining weights represent chemical reactions and systematic relations in the simplest and most convenient manner. The corresponding chemical formulæ are either the simplest possible, or, if not, there are usually satisfactory reasons for regarding the multiple formula as the more suitable one.

The following table gives a survey of gases and vapours of compounds of elements which are themselves unknown in the gaseous state.

	Combining Weight.	Molar Weight Observed.
Methane, CH_4	16·0	16·1
Carbon dioxide, CO_2	44·0	44·3
Silicon tetrachloride, $SiCl_4$	170·2	172·2
Boron trichloride, BCl_3	117·4	117·5
Aluminium chloride, $AlCl_3$	133·5	139·1
Gallium chloride, $GaCl_3$	176·3	177·6
Indium chloride, $InCl_2$	184·6	186·6
Chromyl chloride, CrO_2Cl_2	155·0	160·8
Ferrous chloride, $FeCl_2$	126·9	125·2
Zinc chloride, $ZnCl_2$	136·3	133·6
Cuprous chloride, Cu_2Cl_2	198·1	200·8
Lead chloride, $PbCl_2$	277·8	278·3
Bismuth chloride, $BiCl_3$	314·9	330·4
Thallous chloride, $TlCl$	239·6	255·1
Antimony trichloride, $SbCl_3$	226·7	226·0
Columbium pentachloride, $CbCl_5$	271·5	278·3
Vanadium tetrachloride, $VdCl_4$	193·1	193·8
Tantalum pentachloride, $TaCl_5$	360·3	373·9
Molybdenum pentachloride, $MoCl_5$	273·3	274·2
Tungsten pentachloride, WCl_5	361·1	368·1
Uranium tetrachloride, UCl_4	381·3	385·5
Stannous chloride, $SnCl_2$	189·4	193·3
Stannic chloride, $SnCl_4$	260·3	266·7
Titanium tetrachloride, $TiCl_4$	190	198·3
Zirconium tetrachloride, $ZrCl_4$	232·4	236·2
Germanium monosulphide, GeS	104·3	102·6
Germanium tetrachloride, $GeCl_4$	214·1	215·6
Germanium tetraiodide, GeI_4	579·7	594·1
Potassium iodide, KI	166·0	169·5
Thorium tetrachloride, $ThCl_4$	374·2	359·9

The observed and calculated figures show an agreement mostly very satisfactory, considering the experimental difficulties, and at the same time indicate that the formulæ have the simplest possible form when the molar and combining weights are assumed to be equal.

Among organic compounds, *i.e.* carbon compounds, complex formulæ occur, but they are justified by their chemical behaviour. Here, too, the systematic value of this method is best seen, and so it happened that the development of these considerations first took place in organic chemistry. Ch. Gerhardt (1844) was the first investigator who expressly stated that the most suitable formulæ of compounds are determined by their vapour densities. We owe to Cannizzaro (1858) the convincing proof that a similar choice of the combining weights of the elements leads to a simple and convenient notation in the other branches of chemistry.

When we take molar weights of different substances into account in chemical reactions, we have to work with definite quantities, and therefore refer the originally relative figures to a definite unit, the gram. These numbers then denote as many grams as there are units in the molar weight; the name mol is given to these, the really measurable quantities in chemical considerations. A mol of oxygen is 32 g. of oxygen, and a mol of hydrochloric acid is 36·47 g. Almost all the properties of substances with which we shall be concerned, are referred to these quantities.

Since 1 g. of oxygen in the molar condition occupies 700·38 ccm., 32 g. at 0° and 76 cm. pressure will occupy 22412 ccm. According to the definition, one mol of any other gas will have the same volume at the same temperature and pressure. The volume of one mol of any gas or vapour at a pressure p, and temperature t°, is given by $22412 \times 76 \times (1 + \alpha t)/p$. If the general gas equation, $pv = rT$, is referred to one mol of a gas, we have in r a general constant, which is independent of the gas or vapour. Its value is obtained from $r = p_0 v_0/273 = 76 \times 22412/273 = 82{\cdot}07$, if the pressure is given in cm. of mercury. In absolute units 1013130 is substituted for 76, *i.e.* one atmosphere pressure in absolute units (p. 41), and the constant becomes $8{\cdot}316 \times 10^7$ in ergs/degrees of temperature. This value is usually denoted by the letter R, and the gas equation takes the form in which it will subsequently be always applied. In this form it always refers to one mol of the substance, and R is therefore always $8{\cdot}316 \times 10^7$.

If we recollect that, as previously stated, pv is an energy-magnitude, we see that the volume energy of the formation of one mol of any gas is $8{\cdot}316 \times 10^7 \times T$ ergs, independent of the nature of the gas, provided it obeys the gas laws.

For many purposes it is convenient to know R in other units. The most frequent is in gravitation units, 1 g. per sq.cm. being the unit of pressure. One atmosphere is 1033 units, and $R = 22412 \times 1033/273 = 84800$. If the volume is in litres and the pressure in atmospheres,

$$R = 22{\cdot}412 \times 1/273 = 0{\cdot}08207.$$

It may be mentioned by way of illustration that in the sense of volumetric units, in which a solution is called normal when it contains a gram-formula weight in a litre, gases at atmospheric pressure and 0° are 1/22·4 normal, and at room temperature 1/24 normal.

Avogadro's Hypothesis.—The historical development did not follow the same line as the above treatment; it was aided by a hypothesis, supplementary to the atomic hypothesis. The first conclusion in this direction drawn from Gay-Lussac's law was that equal volumes of different gases contain an equal number of atoms. This assumption was wrecked by the same facts which rendered it impossible to make molar weights and combining weights the same.

To meet this difficulty, Avogadro (1811) and Ampère (1812) extended the atomic hypothesis, making a distinction between the smallest particles of chemical processes, the atoms, and the smallest self-existent particles, the molecules. These are not identical, as at first tacitly assumed, but the molecules may consist of a larger number of atoms. Ampère, on crystallographic grounds, placed this number as at least four; Avogadro, on the other hand, showed from purely chemical reasons that for the elementary gases the molecule need only consist of two atoms.

When Avogadro advanced the statement that there are an equal number of molecules in equal volumes of different gases at the same pressure and temperature, he came to the conclusion that the relative weight of molecules must be proportional to the gas density, and that accordingly the determination of vapour density affords a means of measuring the relative weights of molecules, just as the estimation of the combining weight does for measuring the relative weights of atoms. The idea of molar weight which was deduced above on a purely experimental basis, attains in this consideration the hypothetical significance of molecular weight; and the proof that on the one assumption, the combining weight of a compound can be represented as the sum of the combining weights of its constituents, now becomes a proof that the molecules of compounds can be represented as always containing a whole number of each of the atoms present.

Colligative Properties.—If we glance backwards at the relations which subsist between the volumes and the chemical composition of gaseous compounds, we see that they are of quite a different type from those which came to light when we considered the mass relations of chemical substances. As has been already mentioned, the latter are purely additive, *i.e.* the mass of a compound is the sum of the masses of its elements. With respect to the volume taken up by gases, this property is in a certain sense quite independent of their chemical composition. If we take, for example, a definite volume of hydrogen and transform it into water vapour, its volume is not altered thereby. The water vapour can by combination with ethylene, C_2H_4, be changed into alcohol vapour, C_2H_6O; the volume still remains the same. Ethylene may again be added, so as to give butyl alcohol, $C_4H_{10}O$, without a change of volume occurring; and so on. Properties that always retain the same value for definite groups of substances, independent of the chemical nature and number of the atoms in these complexes, I have, at the suggestion of Professor

Wundt, named colligative. The volume of gaseous substances, therefore, is such a colligative property.

As we explained the existence of additive properties by the atomic theory, which states that in compounds the component elements remain unchanged each after its nature (p. 118), so we now explain the existence of colligative properties by the assumption of molecules, *i.e.* independent atomic groups, which determine certain relations by their number alone and not by their nature or their chemical composition.

If it is made quite clear that the regularities and methodic advantages, which form the basis of the molecular hypothesis, can be developed in a purely empirical manner, the familiar term molecular weight may be used, without committing one to the hypothesis. For scientific purposes a molecular weight of a substance merely means such a quantity that the constant R in the gas equation has one definite value, independent of the nature of the gas. It can only be applied to substances which occur in the state of gas or vapour. It will be shown later that the definition can be extended to dissolved substances. When the attempt is made to assign a molecular weight to liquids or solids which are not solutions, it is necessary to prove whether and in what way the definition applies in the new case. The presence of colligative properties can in general be regarded as such a criterion, since it was these properties which originated the idea.

Abnormal Vapour Densities.—We have till now spoken only of those determinations which conformed to Avogadro's hypothesis that equal volumes of different gases contain the same number of molecules. There have been discovered, nevertheless, a number of substances, though by no means a great number, which appear to form exceptions to the law. However, it has been shown that these exceptions are only apparent, so that, instead of contradicting the theory, they actually confirm it.

One of the best known examples is to be found in ammonium chloride. According to the formula NH_4Cl it has the molecular weight 53·5, and its molar weight ought to be the same; in reality, however, we only find it somewhat more than half this number, viz. 29. The explanation of the inconsistency lies in the fact that the vapour of ammonium chloride does not consist of molecules of NH_4Cl at all, but principally of NH_3 and HCl, into which it has decomposed. The volume is doubled, and the density reduced by half.

The proof that the vapour of sal ammoniac is actually a mixture of ammonia and hydrochloric acid was first given by Pebal in 1862. He showed that on diffusion of this vapour the specifically lighter ammonia diffused much more rapidly than the heavier hydrochloric acid, and that both might be identified by their action on litmus paper. The objections raised against the validity of this experiment have all been subsequently answered. In the same way, *i.e.* by difference in the rate of diffusion, and consequent separation, the presence of decomposition products has been proved for very many other substances that exhibited "abnormal vapour densities." Thus every doubt has been removed that abnormally small vapour densities are due to such decompositions.

Baker has lately proved (1894) in another way that this is correct as regards ammonium chloride, for he has succeeded in determining the density of the undecomposed vapour. Careful exclusion of moisture reduces the rate of reaction between ammonia and hydrochloric acid (both the combination and the decomposition) to such an extent that solid ammonium chloride can be vaporised without decomposition. For this vapour the normal value of the molar weight, 53·5, was repeatedly found.

In particular cases the proof has been given in other ways. Phosphorus pentachloride should have the molar weight 208·3; smaller values, however, are always obtained, which vary greatly with the temperature and pressure and sink so low as 104. That this is caused by decomposition into PCl_3 and Cl_2 may be seen from the colour of the vapour. The undecomposed vapour of the pentachloride has a very faint colour, if any, while chlorine is green. It was found that the vapour from the pentachloride was likewise green, and that the green became deeper the smaller the density grew, *i.e.* the more free chlorine was split off.

Just as the irregularities observed in compounds may be explained by incipient decomposition into simpler components with corresponding increase in the number of molecules, so certain exceptional phenomena in the case of the elements are capable of interpretation in the same manner.

The vapour density of sulphur was found by Dumas to be 384 at 500°, whereas according to analogy the density 64, corresponding to the formula S_2 and the molecular weight 64, was to be expected. When the experiments were repeated at higher temperature by Bineau, and particularly by Deville and Troost, it was found that the normal value 64 was reached at about 800° and remained constant above that temperature. We must, in order to explain this phenomenon, assume that the atoms of sulphur unite at low temperatures to form complex molecules, probably corresponding to the formula S_8, along with S_2 (and perhaps S_4 and S_6) which then decompose at higher temperatures, into the simpler form S_2.

Determinations of the molar weight of sulphur in various solvents give the higher molar weight S_8. On the other hand, the vapour density of sulphur just above its boiling-point varies greatly with the temperature; it is thus already partly decomposed. It therefore seems more probable that at lower temperatures the vapour is a mixture of S_8 and S_2 in varying proportions. It is not clear, from the experiments made so far, whether S_6 and S_4 exist at all.

The changes in the density of iodine vapour observed by Victor Meyer (1880) are still more striking. Up to 500° the density has the value 254, corresponding to the molecular weight 254 and the formula I_2. If the temperature be raised this value continually decreases, until at high temperatures (about 1500°) and under diminished pressure the value 140 is reached, which nearly corresponds to the formula I (Crafts and Meier, 1881).

Similar phenomena have been observed in the case of chlorine, bromine and phosphorus, but the decomposition here is not so extensive.

All these facts demonstrate the suitability of the idea of molar or molecular weight, and its applicability to complicated phenomena. A further test is the fact that vapours for which molar weight and combining weight are the same as *e.g.* mercury, give no indication of change in vapour density at the highest attainable temperatures. From the molecular standpoint, this simply means that molecules which contain only a single atom are incapable of further decomposition.

Surface - Energy as a Colligative Property.—There are other colligative properties besides that of gas-volume (or rather R). But for pure substances only one is known, although there is for dilute solutions a series of related colligative properties. The former is the surface energy and holds for liquids.

If one mol of different liquids is left to itself in a space and the influence of gravity removed, each of the masses will assume the form of a sphere on account of its surface tension. The surfaces of these spheres are the molar surfaces, and the energy required to form them is the molar surface energy.

In the sense of the molecular hypothesis, it may be stated that there is an equal number of molecules in each of these surfaces, since the total number of molecules in the spheres is the same, and the spheres are geometrically similar; at each surface, therefore, there is the same number of molecules.

Now the volumes of spheres are as the cubes of the radii, and the surfaces as the squares. Since the volume is equal to the molar volume, the surface is as the 2/3 power of the molar volume. If this is multiplied by the surface-tension, we obtain the molar surface-energy, a magnitude analogous to pv, the volume energy of gases.

If V is the molar volume and γ the surface tension, the molar surface energy is $V^{2/3}\gamma$, the general numerical factor $\sqrt[3]{36\pi}$ being omitted.

Eötvös (1886) and Ramsay and Shields (1892) have found the following laws for the molar surface energy.

The molar surface energy decreases proportionally with the temperature, becoming zero at the critical point. The temperature coefficient is the same for all homogeneous liquids. If w_t is the molar surface energy at the temperature t, and w_0 that at 0°, the equation

$$w_t = w_0' - Bt$$

holds, the coefficient B being independent of the nature of the liquid.

The similarity of this equation with the gas equation is still more apparent, if the temperature is counted backwards from the critical point or the zero value of molar surface energy. Denoting these temperatures by D, the molar surface by ω and the tension by γ, the equation becomes

$$\gamma\omega = BD,$$

which corresponds with $pv = RT$.

B in absolute units is 2·12.

It should be stated that this equation does not exactly represent the facts. The molar surface energy is not quite linear near the critical point, so that the temperatures ought to be reckoned from a point a few degrees below the critical temperature.

The molar surface energy is thus a colligative property like the vapour density (p. 165). The quantities so defined stand in the same simple relation to the chemically comparable quantities, as do those defined by the vapour densities, and this property serves to establish the "molar weights" equally well. The molar weights obtained in this way are in many cases proportional to those given by the vapour density, or the same if the constant is suitably chosen. From the molecular point of view, the determination of the surface tension is a means of estimating the molar weights of homogeneous liquids, just as molar weights of vapours can be estimated from the vapour density.

The principles of the two methods are independent, and it was not to be expected *a priori* that the results would be the same. That they are so is evidence of a very remarkable natural law.

It has been found in the course of the investigations that all substances do not obey this simple law; the deviation from it being that B comes out less than 2·12. The normal value can be retained by the same process as was adopted to "explain" the abnormal vapour densities. All the values in the equation for molar surface energy are experimentally ascertained except the molar weight; if B diverges from the usual value, the molar weight can be so chosen that the normal value is restored. If B is found too small, the molar weight must be increased, to restore B to its usual value. From a molecular point of view the substance in the liquid contains compound or associated molecules instead of the simple molecules which it forms in the vapour state. It is assumed that in normal liquids the molar weights determined from the surface tension are the same as those determined from the vapour density.

The propriety of this conception is made evident by the fact that many substances which are shown by this method to be associated, show signs of associated molecules even in the vapour. This is particularly so with acetic acid, whose molar condition in the liquid is given by the formula $(C_2H_4O_2)_n$, in which n varies between 1·3 and 2·1 according to the temperature. Further evidence is afforded by other methods of determining molar weights in dilute solution (see under); a tendency to form complex molecules is often recognisable in cases where the surface tension points to the same conclusion.

In this class of polymerised liquids are the alcohols, with n approaching 2·6, the fatty acids, some ketones, nitriles, many inorganic liquids, water in particular, for which n goes from 1·7 at 0° to 1·3 at 140°.

The hydrocarbons and their halogen derivatives, the ethers and esters are normal, as are also many inorganic liquids, acid chlorides and anhydrides, sulphur compounds, aniline, pyridine, quinoline, etc.

CHAPTER VIII

DILUTE SOLUTIONS

General.—Strictly speaking, solutions belong to the next division of this work, which deals with the relations between two or more substances, while this book is devoted to pure substances as individuals. Still it seems appropriate to take up dilute solutions now. For in the state of dilute solution substances acquire colligative characteristics which allow the state of solution to be regarded as a special form, analogous to the gas state. The relations to be developed are really the simplest limiting cases of the more general laws regulating the equilibrium between two or more substances; but the simplification introduced by dealing with dilute solutions alone is so great, and the laws are so important, that a previous knowledge of the limiting case is the best aid to a complete understanding of the general subject.

The condition of substances in solution has frequently been regarded as more comparable; and many investigators have expected the simplest results in the case of dilute solutions. But these considerations first attained their present significance when van't Hoff (1886) transformed the earlier vague analogies into a hard and fast theory adapted to numerical application. The fundamental idea of this theory is that dissolved substances follow the same laws as gases. When it is remembered what the simple and general properties of gases have meant for chemistry, leading on the one hand to the idea of molar weight, and on the other to thermodynamics, the enormous significance of the extension of the gas laws to a wider class of substances will be realised. If, in fact, the gas laws in any sense hold for dissolved substances, then, in place of the few substances which can be investigated in the state of vapour, the innumerable substances which dissolve in some solvent or other become to a large degree amenable to theoretical investigation, and with it to prediction of their behaviour.

General chemistry has in the quarter of a century since the theory was enunciated made unusually rapid progress, and chemistry as a whole has made such a considerable advance in its development to the position of a science governed by general laws, as probably never before because of any other single idea. This and the comparative novelty of this advance justify the prominent position given to the theory of dilute solutions.

Osmotic Pressure.—The most important idea, the comprehension of which decisively led to the theory of solutions, is that of osmotic pressure.

When a layer of pure water is brought over any aqueous solution, say one of sugar, the system does not remain in this condition. As in the case of a gas whose density in a given space is not everywhere uniform, the sugar at once begins to rise against gravity and to diffuse into the water, the motion only ceasing when the substance is uniformly distributed throughout the whole mass of water.

This motion may be arrested by bringing between the solution and the pure solvent a septum which will let the latter pass but not the dissolved substance. Such a "semi-permeable" wall can be prepared by saturating a porous earthenware cell first with a solution of copper sulphate, rinsing it carefully out, and then filling up with a solution of potassium ferrocyanide. On and within the earthen wall there is formed a continuous sheet of copper ferrocyanide through which water can be filtered. If we try to filter a sugar solution it requires a much greater pressure, and what passes through is not sugar solution but pure water.

Instead of the precipitate of copper ferrocyanide we may employ many other amorphous substances with the same effect, *e.g.* ferric oxide, silicic acid, tannate of gelatine, and the like. The protoplasm of organic cells is generally clothed with a pellicle which has the same property as such artificially prepared membranes.

If such a prepared cell is filled with sugar solution, and then closed by a stopper which admits of connection with a manometer, we observe an increase of pressure in the interior of the cell to a definite maximum when it is placed in pure water. The maximum value is dependent on the concentration of the sugar solution and on the temperature.

The Laws of Osmotic Pressure.—If the temperature is kept constant, then the pressure is proportional to the strength of the solution (Pfeffer, 1877). The final pressures are very considerable; a one per cent solution of sugar giving 50 cm. of mercury, and a one per cent solution of potassium nitrate a pressure of more than 3 atm.

The proportionality between concentration and pressure is seen from the following measurements by Pfeffer on sugar solutions:—

Concentration.	Pressure.	Ratio.
1 per cent	53·5 cm.	53·5
2 ,,	101·6 ,,	50·8
2·74 ,,	151·8 ,,	55·4
4 ,,	208·2 ,,	52·1
6 ,,	307·5 ,,	51·3

The law that regulates the osmotic pressure has exactly the same form as Boyle's law, for the pressure exercised by gases is proportional to their density or concentration. Recent measurements of Morse have proved this up to 24 atmospheres. It has been shown by many other measurements, both direct and indirect, that the law of osmotic pressure holds for all dissolved substances no matter what their nature.

Temperature has the same influence on osmotic as on gaseous pressure: The pressure increases proportionally with the temperature, and in the same ratio for all dissolved substances. Moreover, this ratio, or the coefficient of pressure, has the same value as in the case of gases.

Thus, if we know the osmotic pressure P_0 at 0°, it will be at t° equal to $P_0(1 + \cdot 00367t)$. The relation may therefore be expressed in the same way as for gases. The osmotic pressure is proportional to the absolute temperature. In proof of this important relation I give the following measurements by Pfeffer and the corresponding values calculated by van't Hoff:—

	Pressure.	At	At	Observed.	Calculated.
Cane sugar .	54·4	32°	14·15°	51·0	51·2
,, .	56·7	36°	15·5°	52·1	52·9
Sodium tartrate	156·4	36·6°	13·3°	143·2	144·3
,,	98·3	37·0°	13·3°	90·8	90·7

The values were calculated on the assumption that the coefficient is ·00367. The differences are not greater than might arise from errors of experiment.

From experiments with living cells it has been also proved that solutions that are in osmotic equilibrium with the cell contents at 0° remain so at 34°. The increase of pressure was shown in this way to be always the same, however different the solutions employed might be, and however complex the cell contents.

The Constant R.—We can thus represent the osmotic pressure of substances in solution by the same general formula as we employed for gases, viz. $pv = RT$. The question now arises, what value the constant R will have in the case of solutions, it being always the same for equimolar quantities of different gases. It has already been calculated (p. 163) for gases and found to be $8{\cdot}316 \times 10^7$ in absolute units.

Now Pfeffer found the pressure to be 49·3 cm. of mercury for a one per cent sugar solution at 0°. The molar weight of sugar, $C_{12}H_{22}O_{11}$, is 342; the volume in which 342 g. of sugar are contained is therefore 34200 ccm. The pressure of 49·3 g. of mercury is equal to $49{\cdot}3 \times 13{\cdot}59 \times 980 = 6{\cdot}56 \times 10^5$. The temperature 0° C. is 273 in the absolute scale. For sugar the constant is therefore $R = \frac{6{\cdot}56 \times 10^5 \times 34200}{273} = 8{\cdot}22 \times 10^7$. As we see, this agrees with the gas constant within the limits of experimental error.

Consequently, the osmotic pressure of a sugar solution has the same value as the pressure that the sugar would exercise if it were contained as a gas in the same volume as is occupied by the solution.

The gas equation $pv = RT$ holds unchanged with the same constant for solutions, only that p here denotes the osmotic pressure. For this extremely important principle we have to thank J. H. van't Hoff (1886).

The question, if this be the same for other temperatures and concentrations, must be at once answered in the affirmative, as the applicability of the laws of Boyle and Gay-Lussac to solutions has been already proved. We have only now to ask if Avogadro's law holds for solutions, *i.e.* if all other substances besides sugar exhibit the same value for R when molar quantities are considered. The answer in this case also is in the affirmative. It is true that there are very few direct measurements of osmotic pressure, but it has been established by the method with organic cells, already indicated, that solutions of the most diverse substances have the same influence, if these substances be contained in the solutions in the ratio of their molecular weights.

All the comprehensive relations previously developed as to the connexion between vapour density or molar weight and combining weight are thus found applicable to solutions, so we may say in general that the state of substances in solution is in the widest sense comparable to that of gases.

Exceptions.—Certain groups of substances, in particular salts, together with many acids and bases, show variations from these simple relations. The osmotic pressure they exercise is much larger than it ought to be from their molar weight; for potassium chloride it is almost twice as large.

Quite a similar irregularity, it will be remembered, appeared in certain definite cases (ammonium salts, etc.) with the vapour density, *i.e.* the density was smaller or, what is the same thing, the pressure was found to be much greater than it ought to be according to theory. The abnormalities were there explained by admitting the substances to be dissociated, *i.e.* to have split up into simpler molecules. The number of mols was thus actually much larger than that which corresponded to the formula of the undecomposed substance, and therefore the pressure was greater in the same ratio.

It is natural to assume a similar explanation here—to look upon the substances which exhibit similar abnormalities as being likewise dissociated in their solutions. It will be shown later that this assumption is really well founded, and explains not only this phenomenon but a great many others.

Diffusion.—The recognition of the existence of an osmotic pressure between a concentrated and a dilute solution of a substance was directly deduced from the fact that a dissolved substance travels from the place of greater concentration to that of less concentration. The possibility of direct measurement of osmotic pressure lay in preventing this movement. Conversely, a theory of this movement can be based on this idea of osmotic pressure, and affords further experimental test of its validity (Nernst, 1888).

Consider two adjacent solutions with osmotic pressures p_1 and p_2; the dissolved substance (solute) will be driven from the concentrated to the dilute solution with a pressure $p = p_1 - p_2$. The velocity of this motion is proportional to p and also to a coefficient representing a kind of friction which uses up energy. The velocity is so small that the kinetic energy is vanishingly small, and the whole work is converted into heat.

To obtain a measure of this property, the diffusion constant, the quantity of substance which in unit time, 1 second, passes through a cylinder of 1 sq.cm. cross section, and 1 cm. in length, with a unit difference of concentration at the two ends of the cylinder, is determined. This definition holds only after a steady state has been reached in the cylinder. The concentration then diminishes proportionally with the length, counted from the end of greater concentration, and the amount passing through the tube represents a constant stream.

An experiment of this kind can be made by filling up a cylinder, *e.g.* a piece of glass tube, with a jelly of gelatine or silicic acid, the one end being placed in a slowly moving stream of solution of unit concentration, the other end in pure water.[1] After a sufficient time has elapsed, the quantity of substance which has passed through is estimated; it is proportional to the time and the diffusion coefficient. If the tube is not of the prescribed dimensions, a correction must be made; the amount of substance passing is directly proportional to the cross-section of the tube and inversely proportional to its length. The amount actually found for unit time must therefore be divided by the area and multiplied by the length.

The numbers expressed in these units are very small, and it is customary to take the day as the unit of time in place of the second; this increases the coefficient 86400 times. As an illustration of the magnitude of diffusion coefficients, it may be mentioned that 0·312 g. diffuses through a unit cylinder from a 1 per cent sugar solution in 1 day.

In view of the large osmotic pressures of even dilute solutions, the velocity of diffusion seems surprisingly small. The explanation from the molecular point of view, is that a given quantity of substance in a resisting medium experiences a greater resistance, the finer its state of division. A sphere of 2 cm. radius has a cross-section of 4π sq.cm.; if it is divided into 8 spheres of 1 cm. radius, the sum

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[1] Most substances diffuse in jellies at the same rate as in pure water.

of their cross-sections is 8π sq.cm., therefore twice as great, and so on. The total cross-section is inversely proportional to the number of the (geometrically similar) particles[1] formed, $q_1 : q_2 = r_2 : r_1$, and increases rapidly with increasing division. The friction for the movement of the same amount of substance is proportional to the total cross-section.

The diffusion constants do not differ much for different substances; they are in general smaller the greater the molar weight of the substance. If the constants are referred to concentrations expressed in percentages by weight, as is usual, there are two grounds for this decrease. The difference of osmotic pressure for the same difference of concentration by weight is smaller the greater the molar weight; on the other hand, substances with high molar weight diffuse much slower under the same difference of osmotic pressure, as they meet with greater resistance; this again from the molecular standpoint is connected with a greater cross-section of the moving molecules.

The temperature effect is nearly the same for aqueous solutions of different substances; the diffusion constant increases a little faster than the temperature; the increase for each degree between 0° and 20° is about ·023 the value at 20°.

Crystalloids and Colloids.—There are many substances whose solutions have practically the same freezing-point or boiling-point as the pure solvent; their molar weight is therefore very great. They also diffuse with great slowness, and are distinguished from ordinary or crystalloid substances as colloids. Silicic acid, ferric hydroxide, many sulphides of heavy metals and also many metals can exist in this condition; lately it has been found that almost any sparingly soluble substance can be got in the colloid state in a suitable solvent. Very many animal and vegetable substances exist in the colloid state, especially the different albumins, gelatine (which has given the name to the group) and many others.

As mentioned above, most substances, especially the true crystalloids, diffuse unhindered through jellies, *i.e.* through colloid masses, with no appreciable change of rate. But this is not the case with colloids; they are more or less completely retained by septa of other colloids, and mixtures of the two classes of substances can be separated by subjecting them to diffusion through colloid septa. Animal membranes such as bladder, parchment paper, collodion, films of gelatine, serve the purpose (Graham, 1862).

There is a gradual transition between crystalloids and colloids, so no sharp line can be drawn between them, and the ability of septa to allow the former to pass through, and to retain the latter, is a difference in degree only. The velocity of diffusion of certain

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[1] If n_1 and n_2 are the numbers, r_1 and r_2 the radii or in general a homologous dimension of particles, q_1 and q_2 the total cross-sections, the proportions hold $n_1/n_2 = r_2^3/r_1^3$, and $q_1/q_2 = n_1r_1^2/n_2r_2^2$, whence $q_1/q_2 = r_2/r_1$.

crystalloids is very considerably reduced by some of the septa mentioned. As septa between two different concentrations of such a substance, they experience an osmotic pressure, which, however, is only a fraction of the whole pressure; just as a not quite gas-tight wall does not experience the whole pressure of an enclosed gas. All the semi-permeable septa which can be practically prepared are of this nature; they will never be perfectly tight for any substance but will permit it to pass, although it may be at such a diminished rate that the difference between the observed pressure and the theoretical value may be immeasurably small.

Determination of Diffusion Constants.—The use of these partially permeable membranes explains the lack of agreement and the complicated nature of the phenomena at first observed, which under the name of diosmosis, dialysis, etc., were often investigated on account of their physiological interest. Not until Graham (1851) returned to the process of free diffusion previously investigated by Parrot (1815) were the main aspects of the phenomena recognised. By the preparation of almost ideal semi-permeable septa, Pfeffer (1887) laid the experimental foundation on which van't Hoff (1886) built his theory.

The arrangement adopted by Graham was to place a concentrated solution of the substance at the bottom of a cylinder, and a layer of pure water over it. After a long time the upper layers into which the substance had diffused, were withdrawn by means of a syphon, and analysed. Under comparable conditions, the greater the diffusion coefficient, the greater is the concentration, but the two are not directly proportional. The complicated formula, given by Stefan, from which it can be calculated, need not be reproduced.

Determinations of diffusion are in all cases rendered difficult by reason of the convection currents caused by slight alterations of the temperature; these cause mechanical mixture of the layers which falsify the results of pure diffusion. The disturbance is always in the direction that the mixture has gone further than would happen by diffusion alone; and consequently the apparent coefficient comes out too high.

It is a great simplification to maintain at one end of a long column of solvent a constant concentration of the solution (keeping the solution saturated by the addition of the solid). The distance which a definite (just recognisable by some reagent) concentration has advanced is then proportional to the diffusion constant, to the square root of the time and the constant concentration at the end of the column. The same holds for the quantity of substance which has diffused.

Significance of Diffusion.—Diffusion phenomena are of very wide occurrence in nature, and exercise a great influence on the course of natural processes. This is particularly so in plant and animal organisms, in which they partially carry on the transport of absorbed and waste material. As their tendency is to equalise the differences of concentration of all substances, and with them all chemical differences, there must be some mechanism to keep these differences intact wherever they are necessary. This is accomplished by sparingly soluble forms of the chemical compounds (*e.g.* starch) which precipitate from the solution and are no longer diffusible, or by the formation of colloids, which also are incapable of diffusion (like most of the constituents of protoplasm) or finally by the cells being protected by semi-permeable membranes, which do not allow the substances to pass through.

It is to be noticed that in the short intervals of time, such as occur here, the distances accomplished by diffusion are very small. Where more considerable distances are required, some other means of conveyance in mass are in force, and we find convection at work wherever material has to be transported a considerable distance. Instances are found in the blood circulation in animals, movements of sap in plants, the collection of oxygen dissolved in sea-water by the gills of fishes, and there are many more. In these cases diffusion is coupled with convection, the final absorption of the mechanically supplied material being a diffusion process. It is easily proved that so simple an experiment as stirring up a rough mixture to a liquid of uniform concentration is by no means a merely mechanical process of mixing. If there were not diffusion between the layers of different concentration brought together by the stirring, much more time would be required, and the mixing would remain incomplete, as may be easily observed on mixtures of different powders.

Dissipation.—In conclusion, diffusion phenomena belong to a general type which includes heat conduction, electric conduction, viscosity and many other processes. They may be characterised as phenomena which dissipate energy in space, since free energy, capable of doing work, equalises itself without performing any corresponding work; in the last resort it passes into heat. For energy to be convertible, there must be a difference in its intensity. A "conduction" of energy takes place between two places where such a difference exists, tending to obliterate the difference. This process is proportional to the difference of intensity or gradient, and its course with time depends on definite constants which are partly a function of the nature of the material, and partly conditioned by the geometrical form of the conductor.

These analogous processes are grouped together under the analogy of one particular case, that of the flow of a liquid. In using this analogy, it must be remembered that the flowing things in the other cases do not possess anything similar to kinetic energy, and that, in consequence, it only holds when the resistance to the flowing liquid is so great that the velocity is relatively small and the kinetic energy vanishes.

The theory of these phenomena was very completely developed by Fourier (1822) for the conduction of heat. Afterwards it was only necessary to seek out in the other regions the magnitudes corresponding to temperature, quantity of heat, and conductivity for heat, and to substitute them in the equations. This was done by Ohm (1827) for the conduction of electricity, and by Fick (1855) for diffusion.

Vapour Pressure of Solutions.—It is a general experience that the vapour pressure of liquids which contain substances dissolved in them is smaller than that of the pure liquids. The laws of this phenomenon, in the first instance for solutions of non-volatile substances, were ascertained by Babo (1848) and Wüllner (1856). They are to this effect, that the lowering of vapour pressure is proportional to the amount of substance dissolved, and that for one and the same solution, the lowering at any temperature always remains the same fraction of the vapour pressure of the pure liquid at that temperature.

If we thus denote by f the vapour pressure of the solvent, that of the solution by f′, and by g the amount per cent of the dissolved substance in the solution, we have

$$\frac{f-f'}{f}=rg,$$

where r is a constant which represents the relative lowering of the vapour pressure for a one per cent solution.

This law, however, like so many other such, is only an ideal law, to which the actual relations approximate more nearly the more dilute the solutions become. In concentrated solutions we have deviations, corresponding to those of gases at high pressures, and susceptible of a similar explanation.

If we refer the constant r, or the relative lowering of vapour pressure, not to equal weights but to molar weights, we at once find an additional general law, the products of the relative decrease and the molar weight being constant for one and the same solvent. Thus, if we dissolve in equal quantities of a liquid such amounts of different substances as are proportional to their molar weights we obtain liquids with the same vapour pressure. The rule may be stated thus: The molar lowering of vapour pressure produced by all substances in the same solvent is constant.

If, lastly, we compare the relative lowering experienced by different solvents, we find them to be equal when equal amounts of a substance are dissolved in quantities of the various solvents proportional to their molar weights. Here the vapour pressure of the solution is to that of the pure solvent as the number of mols of the solvent is to the total number in the solution.

Now, if G be the weight of the solvent, g that of the dissolved substance, M and m being the corresponding molar weights, then $\frac{G}{M} = N$ and $\frac{g}{m} = n$ are the relative numbers of the mols. If, further, f and f′ represent as above the vapour pressure of pure solvent and of the solution respectively, we have, from what has been already stated,

$$\frac{f'}{f} = \frac{N}{N+n},$$

which can be transformed into

$$\frac{f-f'}{f} = \frac{n}{N+n}.$$

The relative lowering of vapour pressure of any solution is equal to the ratio of the number of mols of the dissolved substance to the total number of mols in the solution.

By using the equations $\frac{G}{M} = N$ and $\frac{g}{m} = n$ we have finally

$$\frac{f-f'}{f} = \frac{gM}{gM+Gm}.$$

The preceding rules were mostly discovered empirically by F. M. Raoult (1887). In the last equation there are, beside the molar weights of the solvent and the dissolved substance, only directly measurable magnitudes. If the molar weight of the solvent in the vapour state is known, the molar weight of an unknown substance can be calculated from the relative depression of the vapour pressure caused by dissolving a weighed amount of the substance in a known quantity of the solvent.

Determination of Molar Weight.—In view of the great importance which attaches to the determination of the molar weight of new substances for ascertaining their constitution and their general chemical behaviour, the practical importance of this equation is readily appreciated. It extends the possibility of estimating molar weights to all soluble substances, instead of volatile ones only. Although half a century ago, when organic chemistry was occupied with the generally volatile compounds of the fatty series, the lack of such an aid was not much felt, still, at the time of its discovery, when research was transferred to aromatic and cyclic compounds of high molar weight which are often inaccessible in the vapour state, it was very welcome.

If the above equation is transformed to show the molar weight of the dissolved substance, we have

$$m = gM(1-\phi)/\phi G,$$

in which $\phi = (f - f')/f$. For dilute solutions ϕ is very small compared with 1, and can be neglected in the numerator; we thus get

$$m = gM/\phi G,$$

which can be applied generally to determine the molar weight from the diminution of vapour pressure.

The experimental process used at first was to determine f and f′ by the static method. Owing to the difficulty and uncertainty of this method it has been replaced by the dynamic method, in which, however, a difficulty is encountered in that very special precautions are necessary in determining the boiling-point of a solution. It has been overcome, thanks to the researches of Beckmann (since 1889), and now a molar weight determination by this method is far easier than the determination of the vapour pressure of a low-boiling substance.

Boiling-point Method.—In this process instead of measuring the pressures at which the solvent and the solution have the same boiling-point, the boiling-points at the same pressure, that of the atmosphere, are determined. If the relation between pressure and temperature are known for the pure solvent, the pressure which it would have at the boiling-point of the solution can be found, and we then have all the data for calculating the relative diminution of vapour pressure.

In Fig. 25, ll is the vapour pressure curve of the pure solvent, ss that of the solution, then f = ac and f′ = ab; ϕ, the relative depression of the vapour pressure is bc/ac.

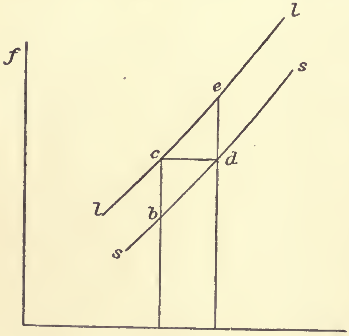

FIG. 25.

The temperature at which the solution boils under the same pressure as the solvent, is found by drawing the line of constant pressure cd. The boiling-point of the solution is necessarily higher than that of the solvent if the vapour pressure is diminished by a foreign substance; this elevation is represented by cd.

If the ratio bc : cd, which is equal to the ratio of the diminution of vapour pressure to the elevation of boiling-point in the same solution, is known, then the latter can be used for finding the molar weight. If s is the elevation of boiling-point and d the (absolute, not relative) diminution of vapour pressure, and the ratio between them d/s = r, $\phi = rs/f$, and the equation $m = gM/\phi G$ becomes $m = gMf/rsG$, or, combining the constants for the same solvent in $K = Mf/r$,

$$m = Kg/sG.$$

The ratio $r = bc/cd$ (Fig. 25) is given by the knowledge of the vapour pressure curve of the solvent. For small differences, ll and ss may be regarded as parallel straight lines; bc/cd is then = ed/cd, which is the change of pressure of the solvent with temperature, dp/dT. Now this ratio is known from the heat of vaporisation (p. 78) and, on the other hand, from the experimental estimation of the vapour pressure curve in the neighbourhood of the boiling-point.

As an illustration of the approximate calculation of the constant K, the figures for ether are given. According to Regnault the vapour pressure of ether at 35° is 76·33 cm., at 40° 90·96 cm. of mercury [1]; the ratio between the increase of pressure and of temperature is $r = 2·926$. In the equation $K = Mf/r$, M, the molar weight of ether, is 74·1, the pressure $f = 83·6$ (the mean of 76·33 and 90·96). From it $K = 2117$; strict calculation gives 2110.

The practical process of determining boiling-points has been worked out mainly by Beckmann (1889); many other investigators have introduced various modifications. The apparatus most generally used (reproduced in Fig. 26), can be employed for almost all purposes. It consists of a boiling vessel A, in the form of a stout tube with a side tube attached. The thermometer is placed in the boiling vessel; the thermometer ends above in a wide chamber bent downwards; by leaving suitable quantities of mercury in this chamber, the thermometer may be used for any temperature within large limits, the scale has a range of only a few degrees, divided into ·01°. The vessel A is partially filled with garnets or clippings of platinum foil to ensure steady ebullition. K_1 is a condenser to prevent loss of liquid.

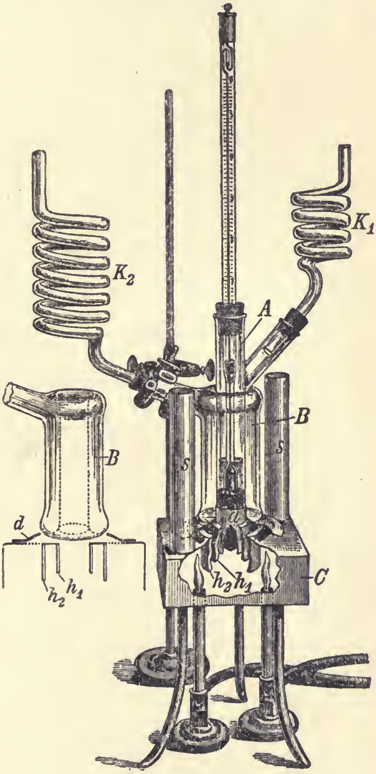

FIG. 26.

The boiling vessel is isolated from the surroundings by the vapour

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[1] Since in the equation for the molar weight, the pressures are present as a ratio only, they need not be expressed in absolute units, as the factor cancels out.

jacket B, in which is a little of the solvent. The heat is so distributed by the heating chamber C of asbestos board that strong but quiet ebullition takes place in both vessels.

A weighed amount of solvent is introduced into the boiling vessel, and the boiling-point observed until it becomes steady. A weighed amount of the solute is then introduced through the side tube (or through the condenser if possible), when the elevation of the boiling-point is soon observed. Other portions of the solute may be successively added and the elevations observed at higher concentrations.

In many cases we can make use of the principle that the vapour pressure is the same in gases as *in vacuo.* If, for instance, a current of air be passed through the solution and then through the solvent, the loss of weight of the first will be to that of the second as $f' : f - f'$, the air being saturated with the vapour up to the pressure f' by passing through the solution, and then further up to f by passing through the solvent. If in addition we determine the weight of the vapour carried over, this is proportional to the vapour pressure f.

If we are working with aqueous solutions, the methods of hygrometry may be employed to determine the relative humidity $\frac{f'}{f}$.

As to the general validity of the above law (p. 178) we find that there are here exactly such exceptions as we met with in the case of osmotic pressure. All substances that gave too high values of the latter, and for which therefore a state of dissociation, decomposition into simpler molecules, was assumed, exhibit quite the same abnormality with respect to the lowering of vapour pressure. The ratio between the actual and theoretical values of the osmotic pressure is equal to the ratio between those of the lowering of vapour pressure. This circumstance strongly supports the assumption that the cause of the abnormalities lies in the dissolved substance and not, as might also be, in the solvent.

Theory of the Diminution of Vapour Pressure.—In view of this complete parallelism between the two series of phenomena—osmotic pressure and the lowering of vapour pressure—we must ask if there is no theoretical connexion between them. Such a connexion actually exists; so that if the laws of osmotic pressure are given we can deduce those of the lowering of vapour pressure from them, and *vice versâ.*

We imagine a vessel of the form of a long cylinder (Fig. 27) which is closed at the top by a semi-permeable wall. Let it be filled with the solvent L and stand in a vessel F also containing the pure solvent. Let some of the solution be placed at L, and the whole now be covered with a bell-jar, and the air be exhausted from this.

The solution will be in equilibrium with the solvent when the difference of pressure corresponding to the column FL is equal to the osmotic pressure. Now the liquid at F and the solution at L are both evaporating; the vapour pressure of the solution at L must therefore be equal to the pressure possessed by the vapour of the liquid at the same place. For, were it greater or less, liquid would either be deposited or would evaporate in h; in both cases the pressure on the semi-permeable wall would change and liquid either enter or leave the funnel. This would go on for ever, so that we could obtain perpetual motion of the second kind, which is impossible.

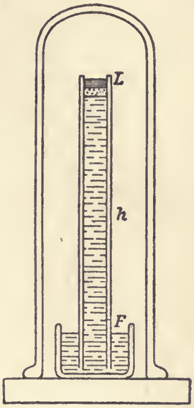

FIG. 27.

The pressure exerted by the vapour of the liquid F at L is equal to the vapour pressure of the solvent diminished by the weight of a column of vapour of the height FL. To this pressure the vapour pressure of the solution must be equal.

We shall now suppose the laws of osmotic pressure to be given. Let the solution contain n molecules of the dissolved substance and N molecules of the solvent. The osmotic pressure (p. 173) is numerically equal to the pressure the substance would exert if it occupied the given space as a gas, *i.e.* by the equation $pv = nRT$, whence $p = \frac{nRT}{v}$. To find v, let us consider that the N molecules of the solvent weigh MN, where M is the molar weight, and occupy the volume $\frac{MN}{s}$, the specific gravity of the solvent being represented by s. We thus obtain $p = \frac{nRTs}{MN}$. The height h of the solvent corresponding to this pressure is given by the equation $p = hs$. Then we have $h = \frac{nRT}{MN}$. Since MN is equal to the weight of solvent that contains n molar weights of the substance dissolved, we can state the rule: The osmotic elevation is, for the same composition by weight, independent of the nature of the solvent.

The vapour pressure f′ of the solution is less than that f of the solvent by the pressure exerted by a column of vapour having the height h, *i.e.* $f' = f - hd$, if d denote the vapour density. This may also be calculated from the equation $pv = RT$; p, the pressure of the vapour, is equal to f, and $d = \frac{M}{v}$ as the formula holds for one mol of vapour. Therefore $d = \frac{fM}{RT}$.

If we now introduce into the equation $f' = f - hd$ the values $h = \frac{nRT}{MN}$ and $d = \frac{fM}{RT}$, it follows that $f' = f\left(1 - \frac{n}{N}\right)$ or $\frac{f - f'}{f} = \frac{n}{N}$. As the result of the experiments by Raoult we found (p. 179) the formula $\frac{f - f'}{f} = \frac{n}{N + n}$. The difference arises from these experiments being made with solutions of finite concentration, while the calculations only hold for infinitely small concentrations; if n is very small compared with N, both formulæ give the same result.

The Freezing-Point of Solutions.—Over a hundred years ago J. Blagden (1788), in a research unusually exact for that age, found between the temperatures at which salt-solutions solidify and the strength of these solutions, the simple relation that they are proportional. His work, however, fell completely into oblivion. Rüdorff in 1861 rediscovered the same fact, and in 1871 de Coppet, who confirmed this result, added the rule that different substances of analogous nature depressed the freezing-point by the same amount if they were dissolved in water in the proportion of their molar weights.

The further development of our knowledge of this subject was for a long time arrested by the investigation being confined exclusively to water as the solvent, and salts as the experimental substances.

Only when F. M. Raoult studied, in the first instance (1882), aqueous solutions of indifferent organic substances, was the simple law ascertained that equimolar solutions (such as contain, *i.e.* in the same quantity of the solvent, quantities of the dissolved substances proportional to their molar weights) have the same point of solidification. When other substances were then employed as solvents the same result was found, so that the following general formula may be given.

If Δ be the depression of the freezing-point of the solvent caused by the solution of n mols of the substance in G grams of the solvent, we have

$$\Delta = r\frac{n}{G},$$

where r is a constant, which depends only on the nature of the solvent. If the molar weight of the substance is not known, it can easily be ascertained by determining the depression when g grams of it are dissolved in G grams of the solvent. We have then $n = \frac{g}{m}$, so that the equation becomes $\Delta = \frac{rg}{mG}$, or

$$m = \frac{rg}{\Delta G},$$

from which we get the molar weight.

The constant r, which, as we saw above, is dependent on the nature of the solvent, may be determined by dissolving substances of known molar weight in the liquid and observing the depression. Introducing the values so obtained into the first formula, we get $r = \frac{\Delta G}{n}$.

This law also holds in the first instance only for indifferent substances; salts, strong acids, and bases are exceptional in their behaviour. These exceptions, however, are again closely related to those noted in the case of osmotic pressure and the lowering of vapour pressure; the depressions actually observed are greater than those calculated, and the ratios between the observed and calculated values are the same for the various substances as those found by the other methods.

Method.—The apparatus of Beckmann (1888), sketched in Fig. 28, is the best for the practical determination of the depression of the freezing-point. The glass tube A contains a thermometer D divided into hundredths of a degree, and a stirring rod made of stout platinum wire. A weighed quantity of the solvent is introduced into A, which is then placed in a somewhat wider tube B, used to form an air-jacket between A and the wide outer vessel C, into the lid of which B is fixed. This external glass vessel contains water or a freezing mixture, the temperature of which lies from 2° to 3° below the freezing-point of the liquid. The thermometer is now observed while the liquid is kept constantly stirred, small clippings of platinum being introduced into A to aid in the thorough mixing. At first, in consequence of over-cooling, it sinks below the freezing-point, thereupon suddenly to rise to the correct temperature when the solid substance separates. The freezing-point of the solvent being in this way exactly determined, a known quantity of the substance to be investigated is introduced from a weighed vessel through the side tube into A, the liquid is thoroughly stirred and the experiment repeated. The freezing now takes place at a lower temperature, and the difference of the two temperatures is Δ in the equations.

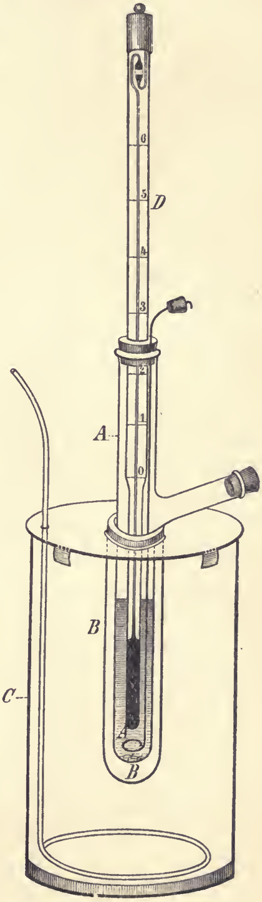

Fig. 28.

With solutions there is often a very strong over-cooling, so that on solidification a large quantity of ice separates. The solution still remaining is thus concentrated, and the observed temperature too low. Most of the ice is then allowed to melt, and when only a small quantity is left the apparatus is again brought into the cooled outer vessel, or the slightly over-cooled solution is "inoculated" with a trace of ice.

Theory.—It is natural to expect between the phenomena of the depression of the freezing-point and the lowering of vapour pressure some such theoretical connexion as we found between the latter and the osmotic pressure. The connexion in fact exists, and was deduced theoretically by C. M. Guldberg (1870). Van't Hoff (1886) completed the theory in several important points, and showed how to derive the constant r from other magnitudes.

First of all we must find an answer to the question whether pure ice[1] is deposited or the solution freezes as a whole. From the experiments made on this subject, and the discussion arising from them, it appears that the former alternative is the correct one. As long as the solution is not so concentrated that the dissolved substance crystallises out owing to the lowering of temperature, pure ice alone separates.

Now the same mode of reasoning as we employed on p. 182 shows that the temperature at which ice can separate from the solution is that at which ice and the solution have the same vapour pressure. Or, in other words, since ice and solution are directly in equilibrium, they must be so if the vapour is interposed, and this must have the same pressure on both sides. If the pressures were not the same, a machine could be made which would constantly transform heat at constant temperature into work, in contradiction to the second law.

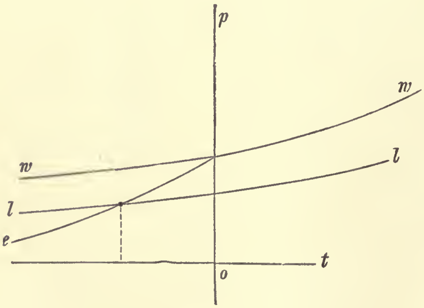

Fig. 29.

From this it follows, therefore, that the laws which we found for the vapour pressure of equimolar solutions also hold for the depression of the freezing-point.

To render the relations which obtain here quite plain, let ww in Fig. 29 represent the curve of vapour pressure for water, the temperatures being the abscissæ and the pressures the ordinates. The curve for ice e has one point (at 0° namely) in common with the curve for water (p. 100). Below 0° the ice curve runs beneath the curve for

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[1] Ice is here used quite generally for solidified solvent, be it water, benzene, or any other substance.

(over-cooled) water. The curve for a solution ll, finally, runs below that for water, so that its abscissæ always form the same fraction of those of water. The freezing-point of the solutions is the abscissa of the point where the curves e and l cut each other, for both ice and the solution, as we just proved, must have the same vapour pressure.

The differences of temperature of which we have here to take account are small enough to justify us in considering the corresponding portions of the curves of vapour pressure as straight lines. It is then clear that the point of section of e and l will move in the same proportion to the left as l sinks under w. Now this sinking, or the relative lowering of vapour pressure has been already found both theoretically and experimentally to be proportional to the strength of the solution, and therefore the depression of the freezing-point must be also proportional to the concentration; which is confirmed by experiment, as we have already seen.

The constant r may be deduced in the following way. We imagine a large quantity of a solution of n mols of substance in G grams of solvent enclosed in a cylinder with a semi-permeable wall. By a pressure on the piston a little greater than the osmotic pressure, so much of the solvent is pressed out as corresponds to the volume in which a mol of the substance is dissolved. The work required for this, if p be the osmotic pressure and v the volume just mentioned, is equal to pv, which in its turn is equal to RT. Let this process be performed at the melting-point T of the solvent. The quantity of liquid pressed out is $\frac{G}{n}$ grams.

We now let this quantity of the solvent freeze, when $\frac{G}{n}w$ calories are evolved if w is the latent heat of fusion of the solvent. We then cool everything by Δ till the freezing-point of the solution is reached, bring the ice into contact with the solution and let it melt. $\frac{G}{n}w$ calories are absorbed, but now at the temperature $T - \Delta$. Lastly, we warm the whole up to T again, so that the system regains its initial state. This process is a reversible cycle of the kind described on p. 78.

The work done by heat in this case is equal to the fraction $\frac{\Delta}{T}$ of the total heat passing from the higher to the lower temperature, where Δ is the difference of temperature and T the absolute temperature of the transformation. In the present case the total heat is $\frac{G}{n}w$, so that the portion $\frac{\Delta G w}{T n}$ is transformed into work. But this work has been found equal to pv or RT, whence $\frac{\Delta G w}{T n} = RT$.

We have therefore

$$\Delta = \frac{RT^2}{w} \cdot \frac{n}{G}.$$

If we compare this value with that given on p. 184 for Δ, it follows that $r = \frac{RT^2}{w}$. The constant r is thus determined by the latent heat of fusion w, and the absolute temperature of fusion.

To illustrate the application of the formula, we will calculate the constant for water. In $r = \frac{RT^2}{w}$, R is $8{\cdot}31 \times 10^7$, $T = 273$, $w = 80$ cal. $= 335 \times 10^7$, from which $r = 1850$.

To test this theoretical result, $r = \frac{RT^2}{w}$, van't Hoff (1887), to whom we owe the calculation, deduced the constants of several substances from the known values of the latent heat and the melting-points, and compared them with the empirically found constants of Raoult. The corrected numbers are:—

	T	w	$\frac{RT^2}{w}$	r
Water	273	79.5	1860	1890
Acetic acid	289·4	43·1	3850	3860
Formic acid	281·5	57·8	2750	2770
Benzene	278·5	30·2	5120	5000
Nitrobenzene	278·3	22·3	6950	7070

If we consider the comparative roughness with which some of the heats of fusion have been determined, the agreement is very satisfactory. The formula was fully confirmed by later researches of Eykman and others.

Summary.—The laws of the boiling-point and freezing-point of solutions are so much alike that the question is forced upon our notice, What is the common cause of this equality? Looking at the theoretical derivation of these formulæ, we find the following.

The molar weight of gases is defined by the work pv, which must be performed when a gas is formed in a space in which the pressure p obtains. This work is independent of p, and is proportional to the absolute temperature and the quantity of gas. If the latter is so chosen that the work is the same for all gases at the same temperature, the quantities are in the ratio of their molar weights.

Since the same laws hold for dilute solutions as for gases, the same definition of molar weight also holds, and since the amounts of work are directly comparable, there is no essential difference between the molar weights estimated by the two methods. If there are differences in the solution, they have the same cause as the differences of the molar weight of the same substance as calculated from the vapour density; *i.e.* they are due to changes in chemical state, polymerisation, or decomposition. Different solvents act on the solute as variation of temperature and of pressure acts on vapours.

If we determine by any method the value of pv for a dissolved substance at one known temperature, we can calculate the amount of substance which brings the constant R in the equation pv = RT to the fixed value of $8{\cdot}316 \times 10^7$ (p. 163). This is a molar weight determination of exactly the same kind as that of finding the requisite values of pressure, volume and temperature for a vapour which satisfies the equation pv = RT.

From this point of view, the three methods are found to consist essentially in ascertaining the same three magnitudes more or less directly. Most direct is the measurement of osmotic pressure. The strength of the solution gives the volume, the pressure and temperature are measured directly.

In the other two methods the temperature is directly measured, the volume is calculated from the strength of the solution. The pressure is indirectly determined, the (osmotic) work being calculated which is done when a small change of concentration occurs; and the formulæ are obtained when this work is expressed by the other magnitudes concerned, especially the latent heat of fusion or of vaporisation.

Any manometer (or pressure meter) is in fact an apparatus which measures pressure by means of work. Take, for example, an ordinary mercury manometer, in which the pressure is measured by the height of a column of mercury. The height is proportional to the pressure, because the work necessary to raise the mercury in a slight rise of the manometer is the same as that performed by the pressure in the simultaneous change of volume in the manometer. There is no manometer in which the pressure to be measured does not produce a change of volume, and therefore perform volume-work, and the theory of any manometer is based on the equality of this work with some other by the performance of which it is itself effected.

By calculating the work done by a change of concentration in the solution, we thus learn the pressure in it, and can fix the third magnitude in the gas equation. In consequence, any process which changes the concentration of the solution will serve for the calculation of the osmotic pressure, if only it can be, theoretically at least, carried out reversibly, and thus the maximum value of the work can be calculated. Any such process can serve as a foundation of a method of determining molar weights.

On the other hand, if the molar weight is known, the work can be calculated with the aid of the osmotic laws for any process which changes the concentration of a solution. According to the second law, the amount of this work is independent of the way it is obtained, provided it is reversible; the calculation of the osmotic work establishes at the same time the amount of any other energy, which can be obtained from the system in the form of work when the solution suffers a known change of concentration (of one or more substances). Hence the laws for the transformation of chemical energy into other forms can be derived, for chemical processes can always be traced back to a change of concentration of the substances present in a given space. Even in instances where there is no direct change of concentration, as in the appearance or disappearance of a solid substance, it is possible from the same standpoint to frame laws for the behaviour under these circumstances. Thus osmotic pressure finds almost unlimited application.

It must not be overlooked in this wide field of applicability that the above laws hold only for dilute solutions, and must be replaced in the case of concentrated solutions by more complicated laws, the knowledge of which is in a very backward state. In fact, these direct and indirect relations deducible from the simple formula are merely limiting laws, which require investigation in each individual case to find out how far their quantitative application is justified.

Salt Solutions.—As has already been mentioned, a large group of substances—acids, bases, and salts, to wit—do not obey the simple laws in aqueous solution. This is no property peculiar to these substances as such, for they behave quite normally and act as calculated from their molar weights. In the same way water occupies no exceptional place with regard to other solvents when indifferent substances are dissolved in it. The exceptional behaviour only appears when the above substances are dissolved in water, and is a result of the mutual action of both factors.[1]

The molar weight of these substances when determined from their aqueous solutions by any of the previous methods is always smaller than it ought to be according to the chemical formula. If M is the molar weight corresponding to the formula, and M_W that found in aqueous solution, we may put $M = iM_W$, where i is a number always greater than 1 and possibly as large as 4 or 5. It is to be noted that all the methods give the same value of i for one and the same solution. A solution of potassium chloride for which i is nearly equal to 2, exhibits not only twice the depression of the freezing-point that corresponds to the formula, but the lowering of vapour pressure and the osmotic pressure are too great in the same ratio of 2 : 1. The number i is therefore not dependent on the method employed, but only on the nature of the dissolved substance, and in a certain measure on the concentration and the temperature.

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[1] It may be well to state here what will be seen later to be of decisive importance for the theory of these phenomena—namely, that solutions which are thus exceptional, and only such, are electrolytes. The two properties are always associated. Besides water, other solvents, *e.g.* acetone, liquefied ammonia, pure nitric acid, etc. possess the same property, though as a rule to a less extent.

The explanation of these phenomena has already been indicated. We must assume that the substances in question are dissociated in their solutions, *i.e.* split up into smaller molecules, just as ammonium chloride is dissociated in the vapour state. It is true that here the dissociation is of a peculiar kind, connected in the most intimate way with the electrical properties of the solutions, as will be shown in more detail in Book IV. on Electrochemistry. At this place it need only be mentioned that, proper consideration of the factor i being taken, the solutions of acids, bases, and salts also obey the general laws of solutions.

Additive Properties.—The whole behaviour of salt solutions is in remarkable agreement with this fact. While it is a characteristic sign of chemical combination that the properties of the components have disappeared in the compound, or are more or less altered, dilute salt solutions exhibit a striking independence of the properties of each constituent, regardless of the nature of the other. All dilute solutions of nickel salts have the same green colour; more exact investigation shows that the depth of colour is the same when equal amounts of nickel are present, whatever acid is combined with it. Similarly, the same colour is observed in all soluble bichromates or permanganates, and the nature of the metal has not the slightest effect on it.[1]

What has been said about colour, is equally true for all other properties of salt solutions. This fact was noticed in an incomplete form by Valson (1874) for the densities of equivalent salt solutions, and was embodied in the so-called Law of "Moduli." If the specific gravities of different solutions containing equivalent quantities of salts in the same quantity of water be so arranged in a table that all salts with the same base come into one perpendicular column and those with the same acid into one horizontal row, the difference between corresponding members of the series in both directions is constant. From this it follows that the specific gravity of equivalent salt solutious is composed additively of two members, one of which depends only on the acid, the other only on the base.

Valson chose a normal ammonium chloride solution (53·5 g. per litre), whose specific gravity is 1·015, as his starting-point and determined the following addenda, expressed in units of the third place, for the calculation of the specific gravities of other solutions—

Potassium .	30	Iron .	37	Chloride .	0
Sodium .	25	Zinc .	41	Bromide .	34
Calcium .	27	Copper .	42	Iodide .	64
Magnesium .	20	Cadmium .	61	Sulphate .	20
Strontium .	55	Lead .	103	Nitrate .	15
Barium .	73	Silver .	105	Carbonate .	14
Manganese .	37	Ammonium	0	Bicarbonate	16

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[1] Some apparent exceptions will be explained later.

Thus if we want to determine the density of a normal solution of calcium nitrate, we must add to 1·015 the constant ·027 for calcium and ·015 for nitric acid, which gives 1·057, agreeing very nearly with experiment.

The same law has been found to apply to all other properties which have so far been examined. In addition to those mentioned above the properties of salt solutions are composed of two factors, one of which depends only on the nature of the metal (or of the metallic radical, *e.g.* ammonium) and the other only on the halogen or other acid radical.

Ions.—In other words, in dilute solution salts behave as if their components were not united; the change of properties which is the sign of combination does not occur. Along with this goes the fact that salt solutions, and these alone, contain, according to the osmotic phenomena, more mols than their formula indicates. We are forced to the conclusion that in dilute aqueous solution salts are not present as compounds but as fractional parts.

What are these fractions? When the salt is composed of two elements, there can be no room for doubt. For sodium chloride they can only be chlorine and sodium, or compounds of these elements with the solvent.[1]

Solutions of sodium chloride do not show any of the properties of elementary chlorine; so we are not justified in supposing it to be present. While chlorine has the formula Cl_2, corresponding to the molar weight 71, the formula of the chlorine in the sodium chloride solution has the molar weight 35·5, and must be represented by the formula Cl. If elementary chlorine really is contained in the sodium chloride solution, it must be an allotropic form of ordinary chlorine.

Similar considerations apply to the other constituent of sodium chloride; the sodium contained in the solution has none of the properties of ordinary metallic sodium, and we consider it likewise to be an allotropic form.

The formulæ of the constituents of compound salts is obtained by analogy. Any sodium compound can contain only this allotropic sodium as one of its constituents, and all the rest is the other constituent. And similarly with chlorides. Alongside the allotropic chlorine are ranged the groups NO_3 from nitrates, SO_4 from sulphates, ClO_3 from chlorates, ClO_4 from perchlorates, while NH_4, ammonium, and the analogous metallic radicals play the same part as sodium.

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[1] It has been occasionally put forward that the fractions interact with the water, hydrochloric acid and sodium hydroxide being present instead of chlorine and sodium. This is opposed to the facts, for when solutions of these two substances are mixed there is a considerable evolution of heat, change of volume, and a series of other phenomena, proving that the two substances cannot remain together unchanged, but interact chemically. Consequently they cannot be formed together in a solution of sodium chloride.

These substances are called, briefly, ions;[1] those analogous with sodium are kations, the others, like chlorine, anions.

The objection may be urged that these ions have never been isolated, and that their existence is therefore purely hypothetical. The answer may be given that the electrical properties of these components or ions make it impossible that they should be accumulated in sufficient quantity as to permit of separate examination; but that owing to those properties chemically equivalent quantities of anions and kations, no matter in what combinations, are always present at the same time in any given solution.

Or it might be answered that the existence of ions is certain, because they exhibit special properties, the sum of which appears as the properties of salt solutions. The fundamental facts of analytical chemistry afford the clearest illustration of this. It contains scarcely a single reaction for individual salts, only reactions for ions. For instance, barium chloride is not a reagent for sodium sulphate or sulphuric acid, but for the ion SO_4, since all salts in which it is found give a precipitate with barium chloride. And in the same way sulphuric acid or rather any salts containing the ion SO_4 is a reagent for the ion Ba, since any barium salt gives the precipitate with sulphuric acid or any other sulphate. These examples might be indefinitely extended.[2]

Salt solutions are thus to be regarded as binary mixtures of their ions. A large number of considerations will show later that beside the facts of osmotic pressure and molar weight, of the physical properties and analytical reactions of salt solutions, the electrochemical behaviour and the chemical equilibrium of salt solutions not only point to the same conclusion, but make it the only feasible one.

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[1] This name originated from their electrical properties, as will be explained later.

[2] For a detailed account see the author's *Wissenschaftlichen Grundlagen der analytischen Chemie*, 4. Aufl., Leipzig, 1904 (or the English translation: *Scientific Foundations of Analytical Chemistry*).

CHAPTER IX

CHEMICAL CONSTITUTION

General.—That the most profound changes which we know, chemical changes, have no effect on the weight and mass of the objects concerned, is the foundation of the laws of conservation (p. 12). Their great importance lies in the fact that through them an equation can be made for any process from which the value of one unknown term can be calculated if the other terms are known. It has already been explained how this led Lavoisier to a very important turning-point in chemistry, the correct theory of combustion.

But this circumstance, that no chemical process changes the total weight of the system, also acts in the opposite direction, so that no definite information as to the character of a chemical process can be obtained from the measurement of this weight. Even the addition of the law of conservation of the elements, which is the foundation of the whole of analytical chemistry, does not materially increase the range, for analysis will not settle whether an object is a chemical compound or a mixture in which the same elements are mechanically mixed, either separately or as various compounds.

Other properties must be ascertained before this can be settled; and they may be different even when the elementary composition is the same. For only the existence of these differences renders it possible to draw conclusions which go beyond the problem of elementary composition.

The first question regarding a given object with which the chemist is confronted, is whether it is a homogeneous substance or a mixture. If the former, the next question is whether it is a pure substance or a solution. If, again, it is the former, the elementary composition comes next, and analysis supplies the answer. Then comes the molar weight, as to which the considerations of the previous chapter gives information. Finally, we have the question of the "constitution" of this pure substance of known composition and molar weight. For substances are known with identical composition and molar weight, but with different properties; there must be some further circumstance on which these differences depend, and these are grouped together under the general name of "constitution." The possibility of recognising differences, when there is no difference of composition, is based on the differences of specific properties and on the chemical behaviour, so there are two sources for the determination of constitution. The latter are incomparably more diverse than the former, and chemical considerations have at all times played the more prominent part in establishing constitution. Specific (or physical) properties have only been drawn on as auxiliaries. Accordingly these chemical relations appropriately form the contents of the present-day text-books, and the physical relations have been assigned to what has often been represented as the auxiliary science of physical chemistry.

For this reason a competent acquaintance with those chemical properties to which the physical phenomena are to be referred is taken for granted. Still, it is natural that in the course of such an examination, light should be thrown on the chemical behaviour, since the simplifying effect of the physical relations is very useful in mastering the problem. The following is a very brief review of the development which the theory of chemical combination has undergone in the last hundred years (the whole problem is no older than this).

The Theory of Chemical Compounds.—Chemical compounds form a class of a special kind, the members of which can, in part, undergo transformation into each other in accordance with definite laws. The regularities governing these diverse transformations might be developed quite independently of any hypothesis regarding the nature of compounds. This would lead to a genetic system of chemical individuals, similar in many respects to the one in use at present, but differing from it in its entire freedom from hypothesis.

At the present time, indeed, only the merest rudiments of such a representation exist (see Wald, 1901), and, if it were made here, the reader would learn a language which, it may be predicted, chemists of the future will speak, but which is nowhere in use to-day.

The whole systematics of chemical transformations have been developed under the atomic and molecular hypotheses. This could not have taken place unless they had been well adapted to the purpose, and had given on the whole a satisfactory representation of the real facts. It has hitherto manifested a sufficient diversity in the most important matters to give natural expression to new facts, which were quite unforeseen at the time of its origin. But it seems as if this adaptability is nearly exhausted, and it is as well to recognise the lesson that the history of science has repeatedly given, that, soon or late, such an end is inevitable.

With this reservation, the main results of research on the constitution of chemical compounds will be developed on the usual lines of the atomic and molecular hypothesis.

Early History.—Of the numerous questions concerning the nature of chemical compounds, Dalton's atomic hypothesis only answered one, that, namely, which asked whether or not the elements exist as such within them. The answer was affirmative. Chemical compounds are complexes formed by the conjunction of elementary atoms. The facts and theories in the first chapter of Book II. (p. 109) gave us information as to the relative mass of the atoms; the molecular theory and the observations on which it is founded made us in certain definite cases cognisant of the number of atoms in such complexes. In the present chapter we shall be occupied with the mutual relations of the atoms within the molecule.

As a matter of fact the question is as old as the atomic theory itself; from the time that compounds were conceived as being composed of atoms, chemists have endeavoured to obtain a clear idea of the mutual relations of these components, although the relation of this question to actual facts was occasionally forgotten.

Electrochemical Dualism.—The first theory of chemical compounds is due, as we know, to Berzelius, who founded it on the phenomena observed by him during the electrolysis of salts. He saw that the acids of the salts of the alkalies (chiefly studied by him) collected at the copper pole and the bases at the zinc pole, and so, according to the old principle of Stahl, that a body consisted of those things which by their union gave it, and which on its decomposition were reformed, he concluded that acids and bases were the components of salts. The known acids and bases on their combination always produced water in addition, but this was supposed to be preexistent in them, playing the part of a base in the acids, and of an acid in the bases; the real acids and bases were the known substances minus this water.

The same principle was at once extended to all other groups of bodies. Oxides too could be decomposed electrolytically, giving on the one hand oxygen, on the other a metal. Berzelius, therefore, looked upon compounds quite generally as being formed of two parts which were held together by electrical attraction, and could be separated by electrical forces. In this way arose the electrochemical system, according to which the binary arrangement holds good step by step in the most complicated compounds. Alum, for example, was supposed to consist in the first instance of potassium aluminium sulphate and water; the latter was a binary compound of oxygen and hydrogen, the former of aluminium sulphate and potassium sulphate. Each of these salts again consisted of sulphuric acid (SO_3) and a metallic oxide, and these two components, finally, were composed of oxygen on the one hand, and sulphur or a metal on the other.

This view, in principle so clear and simple, proved exceedingly useful, although its foundation was false. Potassium sulphate, as we now know, splits up on electrolysis, not into $K_2O + SO_3$, but into

$K_2 + SO_4$, and the principle of the dualistic theory of Berzelius, that only compounds of the same order can unite to form higher compounds, is contradictory to the fundamental phenomenon from which it was deduced.

In spite of this fundamental error, the electrochemical theory has been of the greatest importance in the development of chemical science. By giving a list of substances arranged according to their electrochemical tension, Berzelius laid the foundation of the science of comparative affinity; while the easily understood and rigorous system rendered possible by the theory has eminently advanced the study of chemistry. Even after the discovery of the error contained in the conception of the process of electrolysis, the theory did not fall to the ground, but remained until its inapplicability to a class of compounds not known at the time of its development was made evident. This class is formed by the non-electrolysible organic compounds.

Isomerism.—An earnest consideration of the relative position of the atoms in the molecule only became requisite when facts were made known that could not be otherwise explained by the atomic theory than through different arrangement of the atoms. This is what is called isomerism.

When Wöhler in 1823 analysed cyanic acid, and Liebig in 1824 fulminic acid, it was discovered that both chemists had found the same composition for these undoubtedly different substances. Berzelius, who compared the researches in his *Jahresbericht* indulged in several speculations as to the manner in which one or other of the investigators could have fallen into error, for that such different substances could have the same composition appeared to such a degree unlikely that the possibility was never entertained.

However, in the following year Faraday, in the course of an investigation of the hydrocarbons which had collected in cylinders used for compressing coal-gas, found, besides benzene, a gas (butylene) having the same composition as the well-known olefiant gas (ethylene), but twice as great a specific gravity in the gaseous state. Berzelius familiarised himself gradually with the idea that in reality substances of the same composition could have different properties, and called attention in his turn to the two distinct stannic oxides. Almost every year now added to the number of new substances of the same composition with different properties, until finally in 1830 the racemic acid discovered by Kestner in Thann (Alsace) proved to be in every respect similarly composed to ordinary tartaric acid, although in its solubility, the crystalline form of its salts, and in its reactions it differed indubitably from the latter.

Berzelius then made the recognition of identically composed substances with different properties the general possession of science by giving it the name isomerism. He soon too distinguished between different kinds of this; for such compounds as Faraday's hydrocarbons, which contained the same elements in the same proportions, but a different number (multiple) of atoms, he introduced the name polymeric, while such substances as contained the same number of atoms merely differently "arranged," he called metameric. These very suitable names remain in use at the present day.

The fact of the existence of isomerism has been of the greatest significance for the theoretical form taken by chemistry, for from it followed that not only the number and nature of the component atoms were of decisive influence in what concerned the properties of a compound, but that there was something besides—something hypothetically referred by Berzelius to the atoms being "placed together in different ways." This view was retained in the whole of the coming development of the conception of isomerism, and at first took the form of the assumption of different "radicals" in the compounds. The assumption, it is true, was not made to explain the phenomena of isomerism; quite other facts caused this development of the electrochemical doctrine, but many cases of isomerism could be conveniently explained by the difference of the radicals.

The Radical Theory.—During the great research of Liebig and Wöhler on benzoyl (1832), a number of substances came to be known, all of which contained the atomic complex C_7H_5O, and were derived from the same original material. A special rôle within the compounds was credited to this unchanged portion; its atoms were supposed to be held together by stronger forces than those which bound the variable components. Here was the theory of radicals; those more stable complexes played the same part in complex compounds as the elements in simpler compounds; Liebig even went the length of stating that these radicals were the true elements of organic chemistry. By the heroic investigations of Bunsen on cacodyle, and the supposed isolation of ethyl by Frankland, so much was adduced in favour of the theory of radicals, that it generally came to be considered the only true form for the conception and representation of the nature of chemical compounds.

The want of clearness in the theory as to the character of the stronger or closer binding of the atoms within the radical, and as to how far this differed from the binding of the radicals amongst themselves or with other atoms, was at that time not felt, because then the problems of chemical affinity never entered into any one's mind at all. Indeed, several chemists, following the example of Berzelius, expressly assumed the existence of a special sort of union different from the ordinary kind, and this they distinguished as "pairing" or "coupling."

The Substitution Theory.—While the theory of radicals grew out of the electrochemical theory, and merely applied its fundamental conceptions without alteration to the new units, another mode of viewing the facts came more and more to the front, and was always receiving fresh support. It was advanced by Laurent (1839), alternately taken up and dropped by Dumas, and fiercely combated by Berzelius, although it finally proved to be perfectly justified and in the highest degree fertile. This was the idea of substitution, the notion that single atoms in a compound could be replaced by others, the new substance still remaining analogous to the original compound. Such observations were first made on the action of chlorine upon organic compounds containing hydrogen; a particularly pregnant example being found in trichloracetic acid (discovered by Dumas), in which three hydrogen atoms of the acetic acid were replaced by three chlorine atoms. The close relationship of this acid to acetic acid was especially noticeable in its retransformation into the latter, a reaction discovered by Melsens.

The new theory contradicted the electrochemical theory in two main points. Berzelius could not admit that "electropositive" hydrogen was so replaceable by "electronegative" chlorine that the similarity of the two compounds could be preserved. On the other hand, the assumption of a substitution—of the entrance of one atom into the place of another, was in direct contradiction to the electrochemical principle of binary arrangement. Both these points were energetically emphasised by the upholders of the theory of substitution. The first led to the proposition, that the "position" alone of an atom—not its nature—was of influence on the properties of the compound. In this form the proposition is certainly not true, and at once experienced opposition. A. W. Hofmann was soon able to show from the bromine substitution products of aniline, that, according to the position of the bromine, its properties frequently appeared very much weakened in their influence, although they never disappeared altogether.

While a compromise could here be made between the new and the old views, the idea of the unitary constitution of chemical compounds obtained a complete victory over the binary constitution. This reform was in agreement with the conception of the molecule as described above, and led to the setting up of molecular schemes, the chemical types, which we shall shortly consider more closely.

The law of substitution, meanwhile, was more and more extended. It was recognised that not only chlorine, bromine, and iodine could replace the hydrogen of organic compounds, but that compound radicals possessed the same property. Here the radicals of the old theory are represented as the true substituents, as was especially perceived by Hofmann and Wurtz from their study of the substituted ammonias. At the same time the way was prepared for the distinction between atom and equivalent: one atom of oxygen does not replace one but two atoms of hydrogen on substitution, and has therefore twice the substituting value of the latter.

The Type Theory.—Dumas, on taking up the idea of substitution, soon carried it, as was his wont, to its extreme consequences, assuming that only the arrangement, and not the nature of the atoms, determined the properties of the compounds. The task, therefore, of finding the principal types lay immediately before him. His attempt to fix them was, however, unsuccessful.

It was the later researches of Williamson on the ethers, and of Hofmann and Wurtz on the organic ammonias, that enabled Gerhardt and Laurent to put the idea into a practical form. According to them all compounds were derived from the types of hydrogen $\left.\begin{matrix}H\\H\end{matrix}\right\}$, hydrochloric acid $\left.\begin{matrix}H\\Cl\end{matrix}\right\}$, water $\left.\begin{matrix}H\\H\end{matrix}\right\}O$ and ammonia $\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N$, by the replacement of their hydrogen atoms by other elements or radicals. Later $\left.\begin{matrix}H\\H\end{matrix}\right\}$ and $\left.\begin{matrix}H\\Cl\end{matrix}\right\}$ came to be recognised as the same. To this scheme Williamson added that of the double and triple "condensed" types, and Kekulé introduced "mixed" types formed by uniting two or more different simple types. In these last attempts to bring the schemes into harmony with the facts, we already find a factor which later on became of great importance. In order that the two groups in condensed or mixed types might be held together, an atom or radical had of necessity to be present which could take the place of two hydrogen atoms, and which thus formed the connecting link, one hydrogen atom in each group being replaced by it. Here, then, there appeared for the first time the conception of the polyatomic radical or element as the condition for the holding together of the molecule.

The classification of compounds according to types was of the greatest use to science, for it gave a convenient survey of a large number of substances already known, and indicated methods for preparing new bodies. Nevertheless it was, on account of its purely formal character, no real theory of chemical compounds. Gerhardt, its founder, was quite clear on this point; he again and again reiterated that his formulæ were only to be looked on as functional, not as constitutional. Soon too the theory proved unequal to the task of keeping up with the progress of science.

The system of types was by no means generally accepted, for the chief representatives of the theory of radicals (who admitted the law of substitution, and by its means widened the old views) kept strictly aloof from it. In particular, Frankland and Kolbe sought to arrive at a proper understanding of chemical compounds in quite another way, which took better into account the nature of the elements and the analogies with inorganic compounds. Thus Kolbe was in a position to predict the existence of isomers amongst the alcohols, where in the system of types there was only room for one substance;

and not only did he prognosticate their existence, but also their behaviour. A few years later Friedel discovered secondary propyl alcohol and confirmed Kolbe's prediction.

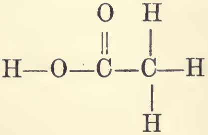
A case of isomerism had thus again shown the necessity of going deeper into the problem of chemical constitution. The experimental basis was discovered by Frankland, and the guiding idea by Kekulé and Couper.

The Valency Theory.—In the course of his researches on organo-metallic compounds (1852) Frankland observed that one atom of zinc, arsenic, antimony, etc., had its combining tendency always satisfied by a definite number of univalent elements or radicals, of whatever kind these might be. In this way was laid the foundation for the study of valency or the capacity of saturation of the atoms.

The application to carbon compounds was not made by Frankland. This important step was taken almost simultaneously (1858) by Couper and Kekulé, who perceived that carbon was quadrivalent, and showed that the constitution of numerous carbon compounds could be explained on this assumption. Every carbon atom can unite with four other univalent atoms or radicals (*i.e.* such as can replace one atom of hydrogen), but not with more. We have chiefly to thank Kekulé for carrying through this idea.

In the theory of valency, which is at the present time the prevalent one, there is thus assumed that each atom possesses a definite limited capacity for combining with other atoms. This capacity is called the valency, and the atoms that can combine with one, two, three, four hydrogen atoms (or equivalent atoms or radicals) are said to be univalent, bivalent, trivalent, quadrivalent, respectively. Carbon is quadrivalent on account of the compound CH_4, oxygen bivalent owing to the compound OH_2. In general, chemical compounds are so constituted that the valencies of the different elements exactly satisfy each other. In acetic acid, whose rational formula is $HO{\cdot}CO{\cdot}CH_3$, one of the carbon atoms is united in the first place to a bivalent oxygen atom with two valencies. The third valency is united with one of the valencies of another oxygen atom, whose second valency is satisfied by a hydrogen atom. Lastly, the fourth valency of the original carbon atom is united with one valency of a second carbon atom, whose three others are satisfied by three hydrogen atoms.

These relations may be made clear by the adoption of Couper's idea of affixing to the elementary symbols as many short lines as there are active valencies, and then joining these from atom to atom. Acetic acid would thus receive the following structural formula:—



$$\mathrm{H{-}O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}{-}H}$$

Such a formula is capable of rendering evident a great many different relations. It shows that one of the hydrogen atoms behaves differently from the others, because it is united with oxygen to form hydroxyl, while the others are all united to carbon. Further, the two oxygen atoms behave differently, the hydroxyl oxygen being more easily attacked and removed than the other. Lastly, the two carbon atoms have different functions; the one, united to two oxygen atoms, easily passes into carbonic acid, the other splits off as methyl, CH_3. All these relations derived from the formula exist in fact; the structural formulæ thus fulfil in a high degree the claim of being both functional and constitutional formulæ.

The valency of hydrogen is usually taken as unity, because, according to all our experience, a single atom of any element can only unite with one definite number of hydrogen atoms, the law of multiple proportions finding no application to the hydrogen compounds that contain only one atom of the other element. Unfortunately, only few elements form hydrogen compounds, so that our ability to fix the valency in this way is limited. We have, nevertheless, arrived at a knowledge of the valency of elements that form no hydrogen compounds, by means of elements or radicals that have been directly found to be univalent with respect to hydrogen. Considerable difficulties have, however, been encountered here, and these are even yet not entirely overcome.

The most remarkable relation of the valencies, as far as they are known, is to be found in the periodic system, for they too form a periodic function of the atomic weight. The valency in the table on p. 154 is constant in the vertical columns, and increases by a unit from column to column. From the fifth column it decreases just as regularly if we take the hydrogen compounds as decisive; the chlorine and oxygen compounds, on the other hand, still show the regular increase.

Here again we see that some elements belong to different rows. As already mentioned, Mendelejeff was the first to call attention to these relations.

Notwithstanding the agreement of numerous facts with the theory of valency, several important difficulties, particularly in organic chemistry, have stood in the way of its being rigorously and consistently carried out. First of all, the primary principle that the combining tendency of atoms is always satisfied by the same number of equivalents is not general. There are many compounds which for a certain quantity of one element have different numbers of equivalents of other elements, as, for example, carbon monoxide CO and carbon dioxide CO_2; nitrogen monoxide N_2O, nitrogen dioxide NO, nitrogen trioxide N_2O_3, and nitrogen peroxide NO_2. Stress must be laid on the fact that these are all substances whose vapour densities are known, so that there can be no doubt as to their molar weights.

Two explanations of this have been offered. The hypothesis of constant valency was by some asserted to be strictly true, and the compounds of an element were called unsaturated when all the valencies attributed to it from a consideration of the majority of its known compounds were not satisfied, the assumption being that in certain circumstances there could be compounds in which some of the valencies remained passive. The reason was not given why this should occur in certain cases only, and why the atoms did not assume the arrangement—always theoretically possible—in which all the valencies would be satisfied. Further, valencies were classed as principal and subsidiary, in order to explain certain comparatively rare kinds of combination.

Other chemists assumed that the valency could change, that in nitric oxide, NO, for example, the nitrogen as well as the oxygen was bivalent. This way of representing the facts is no more an explanation of them than the assumption of unsaturated valencies. Nevertheless, the strife between the supporters of constant and variable valency has been sufficiently bitter.

There still remains, however, one possibility of explaining the actual changes in the valency. If we conceive valency as a consequence of a property of the atoms, its action being modified by differences in their condition, especially by differences in their states of motion, it is comprehensible that although the cause of valency is invariable,. the effect of this cause, the valency itself, may appear different from case to case.

A hypothesis of this kind was advanced by van't Hoff (1878). By assuming that the chemical attraction between two molecules is caused by gravitation, he showed that if an atom possessed a form other than spherical, the intensity of the attraction at its surface would have a certain number of maxima dependent on the form. If the thermal motion of the atom were brisk, only the strongest maxima would be able to retain their atoms, and the valency would thus appear, as is actually the case, smaller at high than at low temperatures.

Molecular Compounds.—The need of finding an explanation for a great class of compounds, mostly known only in the solid state, and whose constitution cannot be explained by the ordinary assumptions as to the valency of the atoms, has led the supporters of constant valency to consider these compounds as being of a different order from those which come under the ordinary rules of valency. These bodies are called molecular compounds in contradistinction to the usual or atomic compounds. The former, which are made to include salts with water of crystallisation, double salts, and (by some) all the salts of ammonia, are not supposed to owe their chemical coherence to the forces acting between atom and atom that condition the valency; but the molecules from which these compounds originate are assumed to exert as wholes such forces on each other as serve to keep the compound together.

The molecular compounds have only been distinguished from the atomic compounds on account of the hypothesis of constant valency—a fact which inclines one to look upon this hypothesis with suspicion, especially as all exertions to find a distinction between the two classes other than that with respect to the valency have proved fruitless. For the rest, the properties of the one class pass gradually into those of the other, a continuous descent from greatest to least stability appearing with corresponding compounds. At present they are commonly explained with the aid of subsidiary valencies (p. 203).

The whole subject of molecular compounds has been recently worked up by A. Werner, acting on the notion of the "coordination number," a generalised scheme of types of compounds. It can be no more than mentioned here.

Stereochemistry.—Structural formulæ have not been found capable of representing all the newly discovered kinds of isomerism, and have undergone extension in a direction which must be regarded as an appropriate development of the principle. After Wislicenus had shown that certain phenomena of isomerism among the lactic acids could not be adequately expressed by structural formulæ written in a plane, van't Hoff (1877) made the first attempt at a space-formulation of the atomic space relations. He imagined the four valencies of the carbon atom to act at the four summits of a regular tetrahedron, and developed the consequences arising from this. One of the most important is that a carbon atom united with four different radicals must be asymmetric, *i.e.* it can exist in two forms, which are not superposable, but are mirror images. The satisfactory agreement of this conclusion with the phenomena of optical activity will be demonstrated in a following section.

A second conclusion, used in diverse ways by Wislicenus to explain and to predict new kinds of isomerism, is the recognition of the fact that a pair of doubly linked carbon atoms, in virtue of the spatial arrangement, gives rise to two isomers of the same structure. The simplest illustration of this idea is the isomerism of maleïc acid (Fig. 30) and fumaric acid (Fig. 31), represented by the adjoining diagrams.

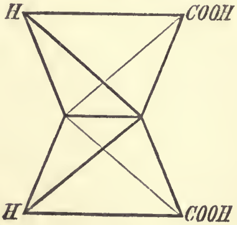


Fig. 30.—Maleïc Acid.

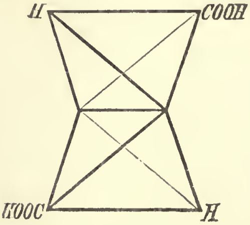


Fig. 31.—Fumaric Acid.

This idea has been exceptionally fruitful, for it not only encouraged chemists, who hitherto had been somewhat shy of these cases of isomerism which were not compatible with structural formulæ, to investigate them more accurately, but served as a reliable guide in more difficult circumstances. In particular the researches of E. Fischer on the sugars are an instance in which the most diverse and complicated phenomena are up to the present very completely and satisfactorily explained by the theory.

In the chemistry of nitrogen compounds also, stereochemistry has been a valuable aid, as Hantzsch in particular has proved. There is already, too, a stereochemistry of compounds of sulphur, selenium, tin, and other multivalent elements.

It appears likely that structural chemistry in space or stereochemistry will go the same way as structural chemistry in a plane. When some such happy idea has been found, soon a large number of facts are found to be in the best of agreement with it. This is necessarily so, because of analogies in the nature of substances which are independent of any particular theory. Also a good symbol proves fruitful in that it predicts phenomena as yet unknown. It is not unlike an empirical formula representing some natural phenomenon, when used for extrapolation. If this is not carried far, there is agreement between the predicted and the subsequently observed fact. If the extrapolation is carried too far, or the near analogies exhausted, the differences become greater, and at last the formula is no longer applicable, and must be replaced by one with more constants which not only represent the earlier known facts, but also those discovered in the interval.

So far the necessary extensions have been possible within the limits of the hypothesis, but it is improbable that this will always be so. Already there are indications from the camp of the organic chemists that structural chemistry is exhausted as an aid to progress.

Tautomerism.—Another necessary development of structural chemistry has been realised without serious change, by the apt use of knowledge gained in other branches of the science. Laar (1885) called attention to a number of substances which behaved as if they had more than one structural formula. He gave them the name of tautomers, and a large number have been since described (they are sometimes called desmotropic). It has been ascertained that they are substances which may easily and rapidly transform themselves into isomers of different constitution. Only one of these forms can exist in the solid state (unless the two forms can separate out as mixed crystals, which is not impossible though it has not been observed); in the liquid state, as the theory of chemical equilibrium demands, they are solutions of the various possible forms. As substances are usually liquid (dissolved or fused) when they enter into reaction, the different forms are always present, and the one form or the other reacts according to the circumstances, the form used up in the reaction being reproduced with a velocity which varies from case to case. From this simple point of view, the nature of the phenomena is readily intelligible, although it cannot be discussed in detail now, as it requires some knowledge of chemical dynamics.

The Three Main Questions.—The increasing complexity of the chemical problems which have arisen out of more exact and more diverse knowledge, has led to numerous questions, which range themselves around three main points. While two of these may be regarded as satisfactorily settled at the present time, the third is still in process of development.

The first point is the appropriate choice of the atomic or combining weight. We shall soon learn the different experiments that have led to a decision of this question, and have finally resulted in a consistent series of atomic weights.

Vapour density has given information about the molar or molecular weight, the second problem, after it was itself definitely established. Development has gone further, for it has been found possible to apply the ideas in cases where the substance could not be examined in the vapour state. "Physical" methods alone are of use here, while the "chemical" methods, which rely on the mutual interactions of substances, are generally of no use.

The third question, that of constitution, is in a different position. It has been from the beginning a purely chemical notion, the components which constitute the substance being those whose existence could be traced through a longer or shorter series of chemical transformations. After these constitutional relations had been established by the chemical methods, search was made for special physical differences among them. Only after such differences had been noticed in known cases was it possible to apply them to unknown cases, though even then with difficulty owing to the undecided question how far the relation is applicable. For this reason the historical development of the idea of constitution has been outlined above, since constant mutual adjustment of physical and chemical methods and ideas are required if the way through this difficult tract is not to be lost.

The Choice of the Combining Weights.—Analysis of suitable compounds of the elements does not fix their combining weights. The numbers according to which the elements can unite are given by it; but there are in addition the rational factors of the law of multiple proportions, and the fundamental stoichiometric laws tell us nothing about these.

If all elements combined with each other in one ratio only, this doubt would be avoided by choosing the combining weights that express this ratio; every compound would then always contain one combining weight of each of the elements in it. But this is not the case; the law of multiple proportions attests that the ratios can be different, and experience teaches us that they are different in the greater number of cases.

There is thus uncertainty, and other relations must be sought if this undesirable freedom is to be restricted so that the "correct," *i.e.* the most suitable, combining weight may be fixed upon.

The atomic hypothesis, which stands in such direct relationship to the law of combining weights, cannot supply this deficiency. It indeed demands that only one of the possible combining weights can be the atomic weight, but provides no criterion by which to decide it.

Berzelius made the first attempt to settle it with the aid of Gay-Lussac's law of the relations between vapour density and combining weight. If the densities of the gaseous elements are proportional to the combining weights or simple rational multiples of them, it is possible to make the two directly proportional, and so make a definite choice. As a matter of fact, Berzelius was the first to enunciate this principle.

He had soon to give it up. For although the elements could be considered in this way, it was not applicable to compounds without abandoning the fundamental rule, that the combining weight of a compound substance is equal to the sum of the combining weights of the elements. These difficulties have been already discussed (p. 159). They have been removed by the development of a new idea suited to the requirements, viz. molecular weight; but this development belongs to a later period.

Berzelius, the most influential of the early investigators, had to be content with a less unambiguous basis. He found it in the two principles of simplicity and similarity, which he strove for in formulating chemical compounds.

The atomic weights were accordingly so determined that the best known and most important compounds received the simplest possible formulæ. The formulæ of substances of similar chemical behaviour were then put into a corresponding form. Iron, for example, gives two oxygen compounds which for fifty-six parts of iron contain sixteen and twenty-four parts of oxygen respectively. The simplest assumption is that in the first oxide equal numbers of iron and oxygen atoms are present, in the second two atoms of iron to every three of oxygen. If we took the atomic ratio 1 : 1 for the second oxide, the first would contain three atoms of iron for every two of oxygen. This seemed less simple to Berzelius, for although the formulæ of the iron compounds themselves would not be rendered more complex, there are a great many other oxides similar to the lower oxide of iron which should therefore, according to the second principle, all contain three atoms of metal to two of oxygen. On the other hand, Berzelius gave to alumina the formula Al_2O_3, which, although less simple than the formula AlO, and not made necessary by the existence of any other oxides of aluminium, is yet to be preferred on account of the great similarity of alumina in its combinations to ferric oxide.

In spite of the uncertainty of this foundation, Berzelius built up with its aid a system of combining weights which has only undergone one material change: the halving of the combining weights of the alkali metals, which Berzelius had made equivalent to the alkaline earths.

Atomic Heats.—While engaged in an extensive research on the laws of heat, Dulong and Petit (1818) discovered one of remarkable simplicity which they stated as follows: The atoms of all elements have the same capacity for heat.

According to the idea of heat-capacity given on p. 35, this means that quantities of the different elements in the proportion of their atomic weights are raised through the same temperature by the same quantity of heat.

The importance of the discovery was at once recognised, but doubts were soon raised as to its general applicability, especially as the undoubted analogy between nickel and cobalt, and between tellurium and sulphur, was called in question by the numbers obtained owing to an unfortunate accident by which the measurements of cobalt and tellurium turned out wrong. The research was not completed as Petit died shortly afterwards, and Dulong did not again take up the matter.

F. Neumann (1831) extended the law by applying it to compounds. His mode of statement is this: The specific heats of substances of similar composition are inversely as their molecular weights, or, what is the same thing, quantities of similarly composed substances in the proportion of their molecular weights have the same capacity for heat.

Numerous investigations into this subject were then undertaken by Regnault (1840) and Kopp (1864). These have in the first instance confirmed Dulong and Petit's, and Neumann's laws within wide limits, but have at the same time shown that both are of only an approximate character. The products of specific heat and atomic weight are equal for very many but not for all elements, the numbers often differing from each other by more than the amount of the experimental error.

With respect to the relations between the atomic heats of the elements and those of their compounds, the principle was enunciated by Joule in 1844, after assumptions made by Avogadro, Hermann, and Schröder had been proved erroneous, that the specific heat of a compound is the sum of those of its components. To Kopp belongs the credit of having proved this law to be of great generality. In other words, the atomic heat is an additive property of compounds. More exact research has shown that this is only approximately true; still it is close enough to permit the calculation of the atomic heat of an element from that of its compounds.

According to Kopp the following elements have a "normal" atomic heat, *i.e.* such a specific heat that when multiplied into the atomic weight gives a number nearly equal to 6·4: Ag, Al, As, Au, Ba, Bi, Br, Ca, Cd, Cl, Co, Cr, Cu, Fe, Hg, I, Ir, K, Li, Mg, Mn, Mo, N, Na, Ni, Os, Pb, Pd, Pt, Rb, Rh, Sb, Se, Sn, Sr, Te, Ti, Tl, W, Zn, Zr.

A smaller atomic heat is possessed by S = 5·4, P = 5·4, F = 5·0, O = 4·0, Si = 3·8, B = 2·7, H = 2·3, C = 1·8 and Be. Only elements of low atomic weight are in this class; those whose atomic weights exceed 30 obey the law of Dulong and Petit.

For several elementary substances it has been proved that the atomic heat increases rapidly with rise of temperature until it attains the "normal" value of somewhat more than 6. Weber found this to be the case for carbon, silicon, and boron, and Nilson and Pettersson for beryllium. Some of the above numbers have not been directly observed, but calculated from the molecular heat of compounds by subtraction of the atomic heats of the other elements.

It was a long time before the atomic heats were systematically applied to the selection of the correct atomic weights. The error in cobalt and tellurium (due to impure preparations, a circumstance which has often since then made the work of physicists worthless) prevented Berzelius from applying it, even to the atomic weight of silver whose compounds he regarded as analogous with those of copper and zinc, but which from the atomic heat should be halved. The same indication as to the alkali metals, found later by Regnault, had likewise no effect. Cannizzaro (1858) first showed in a comprehensive research that the atomic weights deduced from the atomic heats were in accordance with those determined on other grounds which will now be dealt with.

Isomorphism.—The rather vague idea of chemical similarity which Berzelius had at first perforce to make use of was replaced by a more definite notion, at least for a number of elements, when isomorphism was discovered, *i.e.* the fact that some substances crystallise in the same crystalline form, although they are chemically different. This was in direct contradiction to a principle held to be quite general, for at the beginning of last century Haüy advanced as axioms the two principles that each substance had only one definite crystalline form, and that different substances necessarily possessed different forms (except in the regular system, where such are impossible). Both these principles were, however, soon found to be contradicted by experience. Klaproth (1798) had found that calc-spar and arragonite with the same composition have different forms, and this observation was confirmed by later investigations. On the other hand, substances with exactly the same form, such as the alums, the red silver ores, and the mixed vitriols, had quite different compositions. The assumption made to explain this, that the crystals merely contained the foreign substances as admixtures, was disproved by their perfect uniformity and transparency in many cases.

The matter was cleared up by Mitscherlich (1820), who in the course of his researches on the phosphates and arsenates found that these had the same crystalline form when they were of similar composition, *i.e.* when the components were alike except that one salt contained phosphorus where the other contained arsenic. A similar relation was soon found for many other compounds, so that it could be said in general, that the same crystalline form was possessed not only by identical but also by chemically similar substances.

The phenomenon that chemically similar substances crystallise in the same form received the name of isomorphism from Mitscherlich. At first only the similarly constituted substances were called isomorphous, *e.g.* the salts $Na_2HPO_4 + 12H_2O$ and $Na_2HAsO_4 + 12H_2O$. As, however, very many analogous compounds of phosphorus and arsenic are isomorphous, it has become customary to call these elements themselves isomorphous, so that the name is applied not only to those substances having the same crystalline form, but to those elements or groups which can form similarly crystallising compounds with the same residues.

The agreement of the angles of isomorphous substances is (except in the regular system) not at all perfect; strictly speaking, homœomorphism ought to be substituted for isomorphism. The differences are sometimes greater, sometimes less, but can amount to several degrees.

A more certain criterion of the existence of isomorphism than agreement between the angles is furnished by the ability of isomorphous substances to form mixed crystals. In such crystals the isomorphous equivalent components are not in combining but in perfectly indefinite proportions, dependent entirely on the conditions of formation of the crystals. But the sum of the isomorphous elements is exactly equivalent to the quantity corresponding to the formula of either of the simple compounds; or in other words the isomorphous elements replace each other in the ratio of their equivalents.

The properties of such mixed crystals are in general such as would be calculated from the formula of simple mixing. This has been proved for the coefficient of refraction, the specific gravity and the angles. In some cases there occur abnormalities.

Isomorphism has been the cause of numerous theoretical speculations as to the form of the smallest particles, etc., but these have as yet led to no important results. On the other hand, however, the principle of isomorphism has been found exceedingly useful in the discovery and proof of chemical analogies, as just stated. In earlier years the criteria of isomorphism were not strictly observed, and many substances were called isomorphous on the strength of a mere accidental similarity of angle, which may easily happen.

The elements which are either isomorphous or can form isomorphous compounds, are the chemically similar groups, as mainly represented by the periodic system. In fact the empirically classified isomorphous groups are almost identical with these series as a glance at the table on p. 154 will show.

The following points should be borne in mind. The elements of lowest atomic weight are not included in any isomorphous group; the elements up to fluorine stand alone. From sodium onwards isomorphous groups commence, but as a rule the odd and even groups are isomorphous among themselves but not with each other.

Besides these simple relations, there are others whose irregularity is probably due to the imperfections of the periodic system. Lead, for instance, is isomorphous with Ca, Sr, Ba, while cadmium shows closer relations with zinc and magnesium. The metals of the iron group which find no place in the system, and copper in their bivalent compounds are grouped with magnesium and zinc; in the trivalent compounds, so far as they exist, with aluminium, etc. The different valency which many metals assume is the main cause of their belonging to several groups. Thus, manganese in its bivalent compounds is isomorphous with magnesium, in the trivalent state with aluminium. The salts of manganic acid are like those of sulphuric acid and selenic acid, those of permanganic acid are grouped with perchlorates, while the peroxide is isomorphous with the compounds of titanium, zirconium, tin, etc., with the same formula. This element thus belongs to at least five different isomorphous groups.

This diversity is a great advantage for the purpose now under consideration, for by means of it the different groups are linked together. It has led to the requirement that each element is to be given only one atomic weight, which appears correct in all the groups in which it occurs. For example, manganese with the same atomic weight $Mn = 54 \cdot 96$, fits in with every one of the five groups mentioned above, and they are not in contradiction to other similar relations with multivalent elements.

Estimation from the Molar Weight.—Colligative properties are in a certain sense the antithesis of additive properties. While the latter are closely connected with the quantity of substance, the former are so far independent of it that the quantities of substance which have the same value of R in the vapour state, vary widely with the nature of the substance. They have introduced another set of ideas which centre in the molecule as a characteristic unit for chemical affinity and analogy.

The importance of molar weight for the present problem is that neither fractions nor common factors should occur among the coefficients. We have already seen that the first requirement is advanced by the atomic hypothesis (since parts of atoms are a contradiction of ideas), and also from the point of view of stoichiometry, since the deduction of the law of multiple proportions took into account multiples but not fractions of combining weights. The second requirement, that the atomic weight selected be as large as is compatible with the first requirement, is simply a matter of scientific economy. There is no gain, for instance, in putting the atomic weight of carbon at 6, if afterwards all molecular formulæ contain the coefficient 2 for this element. It is simpler and therefore better to make it 12 from the beginning and so reduce all the coefficients to half their previous value.

In this way we get an upper and a lower limit for the most suitable atomic weight. It is not of the same nature as the other criteria. If an atomic heat or an isomorphism has been established, only one single atomic weight can be considered, the possibility of another multiple is simply excluded. But if the molar weights of only a few compounds of an element are known, it is quite possible that accidentally in all these the same multiple of the atomic weight occurs; in which case this multiple would be taken as the correct value, and this error might be rectified by the subsequent discovery of a new compound with another coefficient. This method gives only the highest value, which may possibly be an integral multiple of the correct value. On the other hand, there are the abnormal vapour densities (p. 165) which lead to too small values, unless the complex nature of the vapour is recognised.

Molar weight is therefore an uncertain guide to the best atomic weight; only the circumstance that as a rule a large number of different compounds of the element can be drawn upon increases the certainty against mistake. It thus becomes plain how important even for preparative and systematic chemistry has been the extension of the molecular idea by the discovery of other colligative properties, especially in dilute solutions. It should always be mentioned that Cannizzaro in his research alluded to on p. 209 had already proved from the existing knowledge which at that time was based entirely on the vapour density, that the different methods of selecting the most suitable atomic weights gave the same results.

Other Colligative Properties.—We see, however, at once that the problem can be solved by measuring any colligative property, for by definition all colligative properties assume the same value for equimolar quantities of different substances. If we thus determine how much of the substance with unknown molar weight is required to give a value of any colligative property equal to that given by a known quantity of a substance of known molar weight, then these quantities must be in the ratio of the two molar weights.

Colligative properties have been observed mainly in gases and solutions, and to determine the molar weights of dissolved substances the colligative properties discussed on pp. 178-189 may all serve—thus, the osmotic pressure, the lowering of the vapour pressure and of the freezing-point. The two latter are now experimentally most developed; a determination of the molar weight by the boiling- or freezing-point method is much more easily and rapidly executed than, for example, a vapour-density determination.

The question here arises, in what ratio the molar weights determined according to the different methods stand to each other, in particular whether they are identical. A somewhat comprehensive investigation undertaken by Beckmann (1888) showed that the results obtained by the method of freezing-point depression are in close agreement with those obtained from the vapour density. In one or two cases, where a tendency towards the formation of double molecules is seen in the vapour density, *e.g.* acetic acid, it appeared that different solvents act differently. Dissolved in water, acetic acid exists as normal molecules $C_2H_4O_2$; in benzene, on the other hand, it forms double molecules. The water therefore acts on acetic acid like a high temperature or a low pressure, the benzene like a low temperature or a high pressure. Again, for non-volatile substances, whose molar weights had hitherto only been inferred from the chemical reactions into which they entered, the values obtained from the depression of the freezing-point were almost without exception identical with those obtained on chemical grounds, so that the method holds good on all sides. It should be observed that when a tendency to the formation of double molecules is present, as it is in many compounds containing hydroxyl, effect is much more completely given to this tendency in benzene solutions than when the substance is dissolved in water, acetic acid, or phenol.

The theoretical considerations given on p. 172 *et seq.*, point to the equality of the molar weights in gases and solutions, in agreement with experience.

By the discovery of the colligative character of the properties of solutions just mentioned, the possibility of determining the molar weights, formerly confined to volatile substances, has been enormously increased, for now it extends to all soluble substances, *i.e.* to almost all that come into the chemist's hands. We see at once how much the investigation of unknown substances is advanced by this. If the molar weight of a new body is known, the possibilities of its rational constitution suffer an immediate and great limitation, so that a choice is materially facilitated.

The vapour pressure and freezing-point methods by no means exhaust the possibilities of molar weight determinations in solution, for there are many additional practicable ways of altering the concentration in a reversible manner (p. 189). There is hardly a practical need to work out these methods, and the other relations mentioned are mainly of service in calculating other numerical regularities, the molar weight being assumed to be known.

Liquids.—A colligative property of pure liquids has been discovered in the temperature coefficient of the molar surface energy (p. 168). The results agree, on the whole, with the other methods. It may be supposed, therefore, that they are theoretically connected. Van der Waals has recently developed the theory (1908).

A further colligative property is Trouton's Rule for the heat of vaporisation. If T is the boiling-point of the liquid in degrees absolute, and W the molar heat of vaporisation, $W = AT$, where A is a constant independent of the nature of the substance. At atmospheric pressure A is about 20 cal or 83·7j, or roughly 84j, the formula then runs $W = 84Tj$.

This equation holds for the comparison at atmospheric pressure only, and must not be regarded as a general formula. It does not hold for all temperatures, as is easily seen from its not giving $W = 0$ at the critical temperature, as it ought to do. The coefficient 84 is thus a function of the pressure, which is in the meantime unknown. Deviations from the formula indicate abnormality of molar weight.

Further regularities are afforded by the critical constants and the theorem of corresponding states. They have been discussed by Guye (1894), Ramsay (1894) and others, and give results, as a rule, in agreement with the surface tension method. They are less definite, however, and this mention of them must suffice.

Solids.—Attempts have been made in the following manner to obtain some idea of the molar weight of solids. There are solids of variable composition to which the idea of solution can be applied. They are the isomorphous mixtures, palladium-hydrogen and similar things, and those uniform mixtures which are formed when two non-isomorphous solids crystallise together, a large number of which are known. All these have a claim to the term solution on account of their homogeneous nature. By applying similar considerations as those which led to the various methods of molar weight determination in liquid solutions, to the properties of these mixtures some conclusions have been drawn regarding their molar weight, which, following van't Hoff, are treated as solid solutions.

The results of this attempt, which appear to some extent doubtful, go to show that the molecules in a solid solution are not particularly complex; the molar weight as calculated being generally the same as for liquids. This does not exclude the possibility of other solids being highly complex; solid sulphur, for instance, can hardly have a smaller formula than dissolved sulphur, and this can be as high as S_8.

Polymorphism of solids was frequently looked upon as evidence that the molecules of solids are very complex, as the different forms could only be explained by different combinations of the chemical molecules.

When allotropic solids are brought into the liquid or gaseous state, not a trace of difference between them is left. The vapour of red phosphorus is identical with the vapour of yellow phosphorus. A solution of red phosphorus is different from one of yellow, and the allotropy is retained in the state of solution. A solution of rhombic sulphur in carbon disulphide is in no respect different from a solution of similar composition made from monosymmetric sulphur. But differences persist for some time when amorphous sulphur is dissolved. Conversely, from the same solution, *e.g.* one of nickel sulphate supersaturated by cooling, any one of the different forms of the salt may be obtained by the introduction of a fragment of the corresponding crystal. The so-called physical isomerism thus occurs mainly in connection with the solid substance, and generally disappears whenever the latter assumes another state of aggregation.

While these phenomena may be interpreted in favour of a greater complexity of crystal-particles in comparison with the chemical molecules in liquids or vapours, the results from solid solutions do not point to it.

Results.—Cannizzaro (1858) showed that all these methods lead to the same results, in contrast with the diverse practice at the time. The law of Dulong and Petit had been made good by the more accurate determinations of Regnault (except for the elements with small atomic weight), and the fundamental rules of simplicity and similarity have survived as fully satisfying the requirements of the molecular theory.

These methods have made it possible to exercise an unexceptionable choice from the possible values, a choice which is in every case now generally accepted. The more recently discovered methods have served only to confirm the resulting system.

Hydrogen, $H = 1{\cdot}008$ serves as starting-point.

Oxygen, $O = 16$, from the proportion by volume 1 : 2 with hydrogen on the formation of water; from the equality of its atomic heat with that of hydrogen in the gaseous state.

Nitrogen, $N = 14{\cdot}01$, from the proportion by volume 1 : 3 to hydrogen on formation of ammonia, and to oxygen in the corresponding compounds; from the equality of its atomic heat with that of gaseous oxygen and hydrogen.

Carbon, $C = 12{\cdot}00$, from the vapour densities of both organic and inorganic compounds there has never been found a smaller molar weight than corresponds to $C = 12$. The specific heat gives no definite information.

Chlorine, $Cl = 35{\cdot}46$. From the proportion by volume 1 : 1 on combination with hydrogen; from the volumes of the oxygen compounds.

Bromine, Br = 79·91, and Iodine, I = 126·93, are perfectly analogous to chlorine in their compounds, as well as isomorphous with it.

Fluorine, F = 19·0 was with some uncertainty determined from the analogy with the chlorine compounds. More recently, it has been confirmed by the gas density of the element and of many of its compounds.

Sulphur, S = 32·06, from the vapour density, the volume of hydrogen sulphide, and from the specific heat.

Selenium, Se = 79·2, is isomorphous with and analogous to sulphur.

Tellurium, Te = 127·6, is isomorphous with and analogous to sulphur and selenium.

Phosphorus, P = 31·0, from the specific heat (somewhat uncertain). From the vapour density of the element itself we should conclude that it possessed double this atomic weight, but the vapour density of hydrogen phosphide, on the other hand, gives P = 31.

Arsenic, As = 75, from the specific heat, the vapour density of the trichloride, and the isomorphism with phosphorus.

Silicon, Si = 28·24. The specific heat yields uncertain information: from the vapour density of the tetrachloride, and from the isomorphism with titanium and zirconium.

Boron, B = 11·0, from its volatile compounds.

Lithium, Li = 7·03, from the specific heat, which is normal notwithstanding the low atomic weight.

$$\left.\begin{array}{ll}\text{Sodium,} & \text{Na} = 23{\cdot}00\\ \text{Potassium,} & \text{K} \ \ = 39{\cdot}10\end{array}\right\}\text{from the specific heat.}$$

Rubidium, Rb = 85·4, is isomorphous with potassium.

Cæsium, Cs = 132·8, is isomorphous with potassium and rubidium.

Glucinum, Gl = 9·11. This element has caused much trouble. Corresponding to the low atomic weight, the specific heat is very small, and an indubitable isomorphism has not yet been shown to exist. A determination of the vapour density of the chloride has decided the question.

$$\left.\begin{array}{ll}\text{Magnesium,} & \text{Mg} = 24{\cdot}33\\ \text{Calcium,} & \text{Ca} = 40{\cdot}12\end{array}\right\}\text{from the specific heat.}$$

Strontium, Sr = 87·6 is isomorphous with calcium and lead.

Barium, Ba = 137·4, is isomorphous with calcium, strontium, and lead.

Aluminium, Al = 27, from the vapour density of the chloride and from the specific heat.

Gallium, Ga = 70. The vapour density of volatile compounds, the specific heat, and isomorphism, all lead to the same value.

Scandium, Sc = 44·1, from isomorphism with aluminium.

Cerium, Ce = 140 }
Lanthanum, La = 139 } from the specific heat.

Praseodymium, Pr = 141, and Neodymium, Nd = 144, have not had their specific heats determined in the pure state. The corresponding measurements on the mixture previously known as Didymium fix the atomic weights with certainty.

Yttrium, Ytterbium, and the other metals of the rare earths, from analogy and isomorphism with cerium, lanthanum, and the didymium metals.

Iron, Fe = 55·86, from the vapour density of the trichloride, the specific heat, and its isomorphism with calcium.

Cobalt, Co = 59 } from the specific heat and the isomorphism
Nickel, Ni = 58·6 } with iron, etc.

Zinc, Zn = 65·4, from the specific heat, isomorphism with magnesium, and the vapour density of the metal and its chloride.

Cadmium, Cd = 112·4, from the specific heat and vapour density.

Copper, Cu = 63·6, from the specific heat and isomorphism with iron, etc.

Silver, Ag = 107·9, from the specific heat, and isomorphism with sodium.

Mercury, Hg = 200, from the specific heat, and the vapour density of the metal and its halogen compounds.

Lead, Pb = 206·9, from the specific heat and the vapour density of the chloride: also isomorphous with calcium, etc.

Thallium, Tl = 204, from the specific heat, the isomorphism with potassium, cæsium, rubidium, and from the vapour density of the monochloride.

Titanium, Ti = 48·1, from the vapour density of the chloride and the isomorphism with silicon and tin.

Zirconium, Zr = 90·6, from the vapour density of the chloride and the isomorphism with silicon, titanium, and tin.

Tin, Sn = 119, from the specific heat, the vapour density of the chloride, and the isomorphism with silicon, titanium, and zirconium.

Thorium, Th = 232·4, from the specific heat and the isomorphism with zirconium.

Vanadium, Vd = 51·3, from the vapour density of the chloride and oxychloride and the isomorphism with phosphorus and arsenic.

Niobium, Nb = 94·2, from the vapour density of the chlorides and oxychlorides.

Tantalum, Ta = 183, from the vapour density of the volatile chlorine compounds.

Antimony, Sb = 120·4, from the specific heat, the vapour density of the chloride, etc., and the analogy with arsenic.

Bismuth, Bi = 208·0, from the specific heat, the vapour density of the chloride, and the analogy with arsenic and antimony.

Chromium, Cr = 52·1, from the specific heat, the vapour density of volatile compounds, and the isomorphism with iron, sulphur, etc.

Molybdenum, Mo = 96·3, from the specific heat (doubtful), the vapour density of volatile compounds, and the isomorphism with chromium.

Tungsten, W = 184·0, from the specific heat, the vapour density of the chlorine compounds, and the analogy with chromium and molybdenum.

Uranium, U = 239·4, from the specific heat, the vapour density of the halogen compounds, and the analogy with chromium, etc.

$$\left.\begin{array}{lll} \text{Gold,} & \text{Au} & = 197{\cdot}2 \\ \text{Platinum,} & \text{Pt} & = 194{\cdot}8 \\ \text{Iridium,} & \text{Ir} & = 193{\cdot}2 \\ \text{Osmium,} & \text{Os} & = 191 \\ \text{Palladium,} & \text{Pd} & = 106{\cdot}7 \\ \text{Rhodium,} & \text{Rh} & = 103 \\ \text{Ruthenium,} & \text{Ru} & = 101{\cdot}7 \end{array}\right\} \text{from the specific heat.}$$

The rare gases, argon, helium, and analogues, all discovered within the last ten years, have given rise to much discussion. No chemical compounds of them are known, and the gas density only fixes a maximum value, since the molar weight may be a multiple of the atomic weight. The only other available means is the ratio of the specific heats, which is 1·67 for the monatomic vapour of mercury. The ratio is the same for these gases. This indicates an unmistakable analogy with mercury vapour, which is independent of any hypothesis; similar formulæ appear to be justified if other indications are wanting. But another indication is found in the periodic law (p. 154), since they can only take their regular place in the table if the atomic weight is made the same as the molar weight.

In this table only the most important data are collected; a large number of other confirmatory relations have been left without mention.

The Periodic Law.—The most striking confirmation of the propriety of the above selection of atomic weights is formed by the regularities which appear when the elements are arranged according to the magnitude of the atomic weights so chosen. The relations have been already shortly indicated (p. 152), and now form a fourth and very important means of determining the true from amongst the possible atomic weights, having given a decisive answer in many cases where the other methods failed or were ambiguous.

To complete what has been already said with regard to them, we shall now consider a few properties of the elements and of their compounds in their relation to the periodic system. Besides the discoverers (Meyer and Mendelejeff), Carnelley in particular has instituted investigations in this direction, and at present it may be said that almost every well-defined and comparable property appears as a periodic function of the atomic weight.

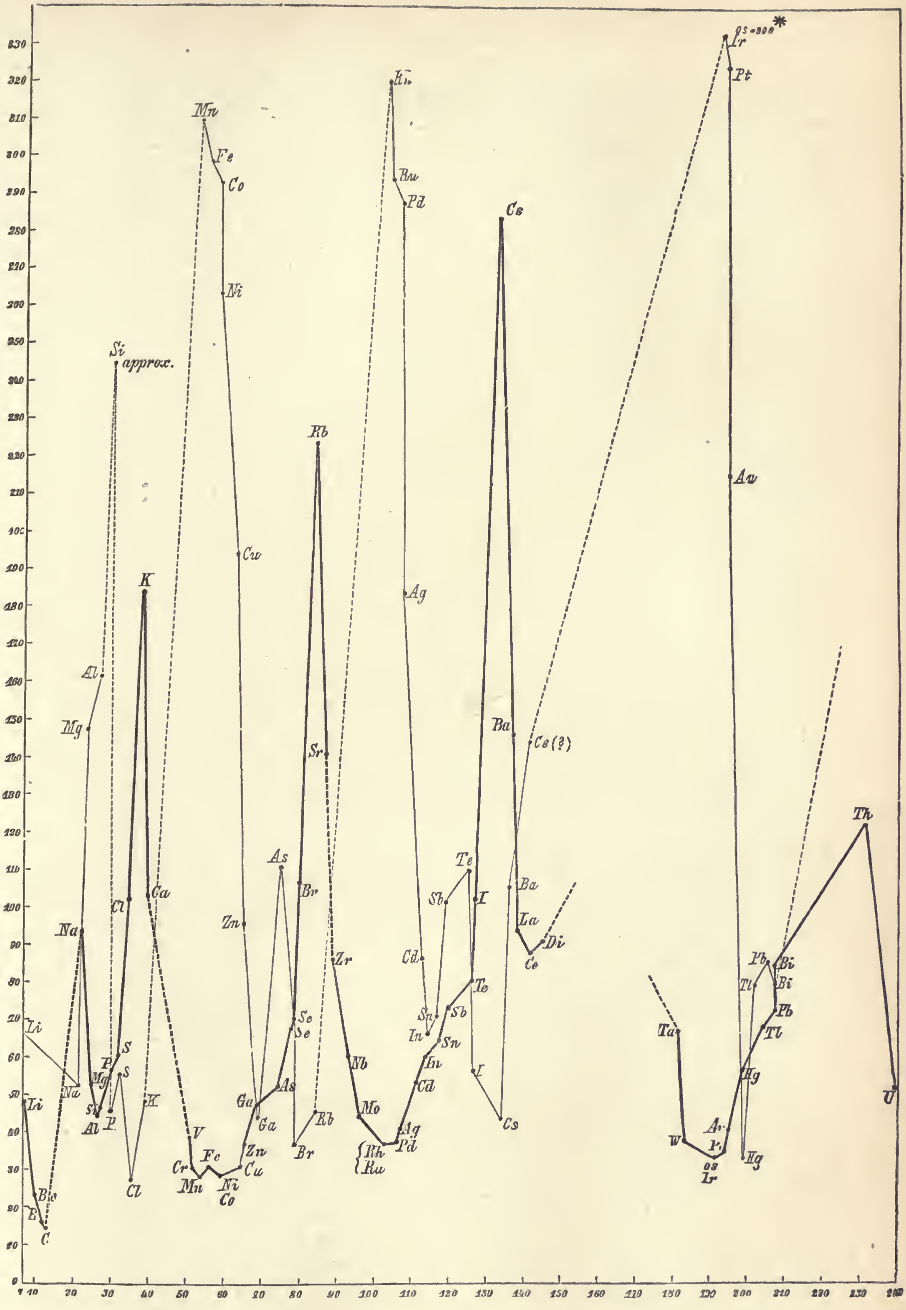


FIG. 32.

The thick line denotes atomic volumes, the thin line melting-points in the absolute scale. The ordinates of the atomic volumes are multiplied by four, the ordinates of the melting-points divided by seven.
* This point should lie 66 divisions higher.

As to the chemical properties, all that is needful has already been stated. Of the physical properties of the elements, the atomic volume shows the periodic variation most clearly, as was first indicated by Lothar Meyer. In Fig. 32 the atomic weights are the abscissæ, and the atomic volumes the ordinates, the points being connected by thick lines. As we see, the curve appears as a series of undulations always growing larger as the atomic weight increases, and exhibits the periodicity in the most marked manner. The elements with similar chemical properties are found at similar portions of the curve; thus the strongly basic alkali metals are always at the maximum points, while immediately before them on the ascending portions the strongly acid-forming halogens find their place. After them, on the descending portions of the curve, lie the metals of the alkaline earths, the metals of the earths, and so on, always with diminishing basicity, while the ascending parts are occupied by the elements with a more acid-forming character.

A second property of equally pronounced periodic character is the melting-point. The corresponding curve is given in Fig. 32 by the thin lines. The undulations are here nearly midway between those of the atomic volume, and show a double periodicity, being alternately large and small.

Further regularities of a periodic nature have been observed in the following properties:—molar volume of analogous compounds, refractive power, heat of formation of analogous compounds, conductivity for heat and electricity, colour, viscosity, etc.

It must also be emphasised that the regularities, so far as they are known, are far from having the sharpness and definiteness desirable. They are not of such a character that one can calculate the properties of an element from those of its neighbours; a rough estimate only can be formed. This, of course, in nowise diminishes the value of the general principle; it only renders evident that important problems are here still awaiting their solution.

Such a problem is the obvious attachment of certain elements to different groups. Thus chromium, from its decidedly basic monoxide, should go with zinc and magnesium; from its alum-forming sesquioxide, with aluminium and gallium; while from its acid-forming oxide it ought to be classed with molybdenum and tungsten: only the last analogy has found a representation in Fig. 32. Copper, by its lower oxide and its insoluble lower chloride, is doubtless related to silver, but mercury from the next group and thallium from the third are much more nearly allied to these metals than sodium or gold; while, on the other hand, cupric oxide would serve to place copper along with magnesium and zinc. Manganese, corresponding to its different degrees of oxidation (MnO, Mn_2O_3, MnO_2, MnO_3, and Mn_2O_7), could be brought into five distinct groups. For these and numerous other facts no expression is given by the periodic system.

It must be further borne in mind that the elements with lowest atomic weight have quite an abnormal character. Mendelejeff has called these the "typical elements," a name signifying just the opposite of what is really meant, for these elements are by no means typical of the groups whose first members they constitute, but rather show a decided tendency to assume the properties characteristic of the next following group. Lithium, for instance, forms a sparingly soluble carbonate and an easy soluble bicarbonate, thus resembling the bivalent metals of the alkaline earths, and not the metals of the alkalies. Glucinum in its behaviour is so like aluminium that until the determination of the vapour density of its chloride it was considered by many chemists as a trivalent element. Trivalent boron, again, in the free state as well as in its compounds, is like no other element so much as quadrivalent silicon. Fluorine is distinguished by forming compounds in which it behaves like a bivalent element. The periodic law is once more unable to give a rational explanation of these peculiarities.

The differences between the progressive numerical values of the atomic weights are by no means the same, but vary as much as cent per cent. This is the case with elements whose atomic weights have been so exactly determined that the hope of later researches bringing the values to equal distances apart cannot be entertained. It may, however, be possible to bring these irregularities into a relation of mutual dependence with others known to exist, and so discover a law regulating them. The periodic system leaves at present the impression that the elements are somewhat irregularly scattered in a regular scheme, so that they in some way do not quite fall into their proper places.

In spite of all this, however, we must not hesitate to acknowledge that the discovery of the properties of the elements and of their comparable compounds being periodic functions of their atomic weights, is one of the most important steps made by scientific chemistry in recent times. The principle has stood the test both in the prediction of the properties of elements at the time undiscovered, and in the indication of errors in the atomic weights previously accepted. We must again emphasise the intimate connection between the periodic system and the other grounds for the choice of the real atomic weights. Every attempt to find similar relations in other systems of atomic weights—Gmelin's "equivalents," for example—has proved abortive, so that the periodic law stands, as a means of determining the true atomic weights, on an equal footing with isomorphism, the law of Dulong and Petit, and the law of Avogadro.

Constitutive Properties.—The number of specific properties recognisable in any given substance is very great, for each kind of energy gives rise to one itself, and in conjunction with other special properties. These are mainly constitutive. This is shown by the circumstance that isomeric substances can be differentiated, which depends on their different properties. As the substances have the same composition, these properties must be constitutive.

This constitutive nature is developed to very different degrees. On one hand, there are the properties which are in the main distinctly additive, with the result that the constitutive influences appear as deviations or irregularities in the additive scheme. There was for long a tendency in science to get rid of these constitutive irregularities as far as possible by means of suitable formulation, and leave the purely additive scheme. In general this has not been successful, and it is scientifically more useful to take such influences for granted and attempt to discover their particular regularities. It is in any case a difficult problem, for constitutive differences do not lend themselves to simple classification. But, since simple and important regularities have been observed in some cases (*e.g.* by a comparison of saturated compounds with benzene derivatives) where there are great and to some extent regular differences of constitution, the problem, however difficult, does not seem to be incapable of solution. In the following sections different properties will be considered in the order of their constitutive character.

The Molar Volume of Solids.—After Gay-Lussac had discovered the far-reaching regularities in the case of gases, the question naturally arose whether they did not hold for the other states of aggregation. The answer given by experiment is in the negative; on the contrary, it has turned out that it is substantially an additive property.

Its constitutive nature was at first more apparent, for it was found on calculation that the volume of a solid or liquid compound is generally different from the sum of the volumes of its constituents. For convenience and clearness in calculation, use is made of atomic volume and molar volume. By atomic volume is meant the volume in ccm. which a combining weight in grams of the element occupies. It is simply the product of the combining weight into the specific volume. In text-books and papers the density is usually given instead of the specific volume, which is its reciprocal, *i.e.* to find the atomic volume, the atomic weight is divided by the density. The corresponding numbers have been already used in the diagram (Fig. 32) on p. 219.

Similarly the molar volume is the product of the specific volume and the molar weight, or the quotient of the molar weight divided by the density.

Now the density and volume change with temperature and pressure, and not in the same regular manner as gases do; it is necessary to find out how this indefiniteness can be removed or allowed for. The effects are, however, so small in solids that they frequently fall below the accuracy with which the volume has been determined. They need not be taken into account, as they cannot in any case alter the main features.

If, then, the volumes are compared simply at ordinary temperature and pressure, it is found that the volume of a compound can stand in one of three relations to the sum of the volumes of the elements. In most cases it is smaller, sometimes much smaller than the sum, so that, for example, in compounds of the alkali metals the molar volume may actually be smaller than the atomic volume of the metal alone. These marked anomalies occur especially where the formation of the compound is accompanied by a very large loss of energy (evolution of heat), for as a rule the change in the nature of a system brought about by a chemical change is proportional to the corresponding change of energy. The atomic volume of potassium is 45·2, that of potassium chloride only 37·4, therefore much smaller.

Less frequently the molar volume is greater than the sum of the atomic volumes. This has been observed in most of the iodides and in some sulphides. The third case, where both are equal, must be accidental, for an exact equality would be entirely destroyed by a change of temperature or pressure, either of which would affect the volumes to a different extent.

The first regularity in this domain was found by Ammermüller (1840), who noticed that cuprous and cupric oxides have the same molar volume if we compare Cu_2O with Cu_2O_2. It is as if one atom of oxygen in the lower oxide occupied as much space as two in the higher. Some other examples also correspond to a similar regularity, but many exceptions were soon found.

The question whether the molar volume of solids could be conceived as in the case of liquids to be an additive property was then carefully investigated by Kopp (1841), and on the whole answered in the affirmative. The molar volumes are approximately sums of terms depending on the nature of the atoms or atomic groups. These partial volumes are, however, firstly not always equal to the atomic volumes of the free elements, and secondly the addenda are only constant within somewhat narrow groups, an indication of constitutive influences. These groups, as is to be expected from what has already been said, are for the most part formed of isomorphous compounds.

In the closest connexion with this relation stands the "parallelosterism" of analogous and isomorphous groups enunciated by Schröder (1859). If we arrange analogous salts (*e.g.* the chlorides, bromides, and iodides of the alkali metals and of silver) in a table, in such fashion that compounds of the same element come into one line, vertical or horizontal, then the differences between the molar volumes of parallel lines will be constant. Thus we find

KCl	37·4	NaCl	27·1	AgCl	25·6
KBr	44·3	NaBr	33·8	AgBr	31·8
KI	54·0	NaI	43·5	AgI	42·0

where all the iodides, for example, have molar volumes some sixteen units greater than the chlorides, and where the sodium and silver compounds differ by from one to two units irrespective of the other component.

The sulphates, carbonates, and nitrates of barium, lead, and strontium form a similar set, yet, as has been mentioned, the regularity is evidently limited to isomorphous groups.

The question as to the relation in which the atomic volumes of the elements in the free state stand to their atomic volumes in compounds has only been very incompletely answered. From the fact that potassium chloride, for instance, occupies a smaller volume (37·4) than the potassium contained in it (45·2), we see that some elements decrease considerably in volume when they enter into combination. The assumption is made by Schröder that the volume occupied in the compounds is a rational fraction of the atomic volume when any condensation takes place. Some facts may be very well represented by such an assumption, but it is not at present possible to form a clear conception of the statement that a component of a solid occupies a definite volume within it.

If we assume that silver in silver chloride occupies the same volume as it does in the metallic state, viz. 10·3, then there remains 15·3 over for the chlorine; deducting this number from the volumes of potassium and sodium chlorides we get the numbers 22·1 and 11·8 respectively. Now, the volumes of potassium and sodium in the free state are 45·2 and 23·8, which are nearly twice as large as the volumes of the metals in combination calculated on the above assumptions.

These relations cannot be extended without strain.

Volume Relations of Liquids.—The first regularities amongst molar volumes were discovered by Kopp (1842): equal differences in composition correspond to equal differences in molar volume. Now the molar volumes of the organic compounds, which are here chiefly considered, are dependent largely on the temperature, and before any comparison could be instituted it was necessary to decide at what temperature it should be made. Kopp soon found that far greater regularity was obtained by comparing the liquids at their boiling-points, rather than at one and the same temperature, say 0°.

Kopp followed up his discovery of the above rule by a long series of exceedingly careful experimental investigations, which served partially to confirm and extend his first observations, partially to restrict them. Generally speaking, the molar volume at the boiling-point is an additive property; the molar volume of a compound is the sum of the molar volumes of its components. At other temperatures, relations of this kind are not so noticeable.

In homologous compounds the molar volume changes for every CH_2 by 22 units on the average. This was proved for the hydrocarbons, alcohols, esters, acids, aldehydes, and ketones.

Isomeric liquids have the same molar volume, as was shown in particular by the comparison of isomeric esters and acids.

When two atoms of hydrogen are replaced by one atom of oxygen the molar volume is not materially altered. This holds specially for the change of alcohols into acids, but also in other cases.

One atom of carbon and two of hydrogen can replace each other without the molar volume suffering any change. This relation was verified exclusively by the comparison of fatty and aromatic compounds.

These rules at once lead to the idea of ascribing definite atomic volumes to the elements carbon, hydrogen, and oxygen, of which all the compounds mentioned above are composed, so that the molar volume of the compound may appear as the sum of these atomic volumes. This has proved to be not quite possible, however, the deviations being too large. The property in question is thus not purely additive. Kopp showed how the different modes of combination of oxygen stood in relation to these deviations. When the oxygen is doubly linked to one carbon atom (carbonyl oxygen) the molar volume is larger than when it is singly linked to the carbon atom (hydroxyl or ether oxygen). If we thus ascribe different atomic volumes to oxygen according to its chemical function, the molar volumes of the compounds can be represented as the sum of the atomic volumes of their elements, with an error of at most four per cent.

The numerical values of the atomic volumes are :—

Carbon	11
Hydrogen	5·5
Carbonyl oxygen	12·2
Hydroxyl oxygen	7·8

We have here, then, a constitutive influence which was at first regarded as additive. The irregularities still remaining show that this process has not quite attained its end, or, in other words, the constitutive influence is not constant.

Kopp also fixed the atomic volume of other elements as follows :—

Sulphur	22·6	Silicon	32
Chlorine	22·8	Arsenic	26
Bromine	27·8	Antimony	33
Iodine	37·5	Tin	40
Phosphorus	25·4	Titanium	35

The last numbers are rather uncertain, as they were derived from only a few compounds.

Very different results were obtained for nitrogen according to the nature of the compounds investigated; no satisfactory explanation has been given of this. The sulphur compounds also exhibited in many cases considerable deviations. Here the constitutive influence is large and variable.

Thus Buff (1865) showed that unsaturated compounds have always a somewhat larger molar volume than that calculated from Kopp's numbers. The same result was afterward obtained by Schiff and Horstmann. The latter also showed the great influence exercised by the chemical constitution in another direction, viz. by the so-called "ring"-formation.

The later development of the subject was hindered for a long time by the attempts of investigators to retain the additive form of regularity. For this purpose they assumed special series of constants, different values of atomic volume in different groups, etc., in order to include the actual deviations from the simple sum of Kopp's formula, in an expression of the same type. All these attempts failed; in spite of this they are still kept up by a few.

It has only come to be recognised lately that the molar volume is not a purely additive property, but constitutive. It must be said, however, that there never can be two cases in which formally identical chemical changes on two substances are really exactly equal. Consider the substitution which exercises the smallest and most regular effect on the chemical properties, the exchange of hydrogen for methyl. The substances formed by this process are called homologous because of the smallness of this effect.

While, for example, the transition from an alcohol with twenty or more carbon atoms to the next higher homologue exerts such a slight influence that the two are scarcely distinguishable by virtue of their chemical properties, the change becomes greater the smaller the number of carbon atoms, and is a maximum for the change from methyl to ethyl alcohol. And the same is true for all similar cases. In general, then, the same substitutions (or any other chemical change) in different substances are not strictly equivalent. There are, therefore, never two exactly equivalent constitutive differences and the constitutive influence of analogous chemical differences can never be exactly the same.

The problem is therefore not that of establishing a rigid formula, but of showing the parallelism of the diverse constitutive differences and the deviations of the molar volume from the simple scheme. Very little work has as yet been done in this direction.

The above considerations have been worked out on the molar volumes measured at the boiling-point at atmospheric pressure. It may be asked if these temperatures are comparable. The only reasonable ground of criticism is van der Waal's (p. 71) theorem of corresponding states. According to it the volumes are comparable, not at the boiling-point at the same pressure, but at equal fractions of the critical pressure. That regularities have been observed at the ordinary boiling-points may be due to the circumstance that the critical pressures are not widely different, and therefore the boiling-points at equal pressures are not very far from corresponding states.

Investigations on the molar volume at other temperatures and equal vapour pressures have in fact shown that the same regularities appear in the same form, but with somewhat different figures. In the few cases in which comparable molar volumes, according to van der Waals, were used for calculation the constitutive deviations from the additive scheme were by no means removed. Although an investigation of the question in this direction would undoubtedly yield many valuable results, it would make the general scheme more sharply defined, but hardly anything more. It should be remembered, too, that the rule of corresponding states has not proved so far a strict law, but an approximate rule only. Hence there is diminished certainty in applying it to the present case.

Refraction in Liquids.—Light, as is well known, traverses different transparent substances at very different rates. The velocities may be easily ascertained by observing the path pursued by a ray which passes from one medium into another at any angle. The law that the sine of the angle of incidence is in a constant ratio to the sine of the angle of refraction then obtains, and this ratio, called the index of refraction, is that of the velocities of light in the two media.

In isotropic substances, viz. liquids, amorphous solids, and regular crystals, light travels at the same rate in all directions; they have only one refractive index. Uniaxial and triaxial crystals have an infinite number of different refractive indices according to the direction, two or three of them being singular values. The following considerations apply to liquids only.

If we observe the deviation of a ray of white light by a prism of liquid, we obtain as usual a spectrum, in consequence of the colours being differently refracted. The index of refraction must therefore be measured for definite rays. The kinds of light mostly employed are given in the following table, with their wave lengths in millionths of a millimetre:—

Lithium (red)	670·6
Hydrogen (red)	656·2
Sodium (yellow)	585·5 and 588·9
Thallium (green)	534·5
Hydrogen (green)	486·0
Hydrogen (violet)	434·0

The index of refraction of a given liquid is dependent on the temperature as well as on the kind of light, usually decreasing with rise of temperature. It varies also when the specific volume of the liquid is changed by alteration of the external pressure. We must therefore ask if there is no function of the index of refraction which represents the influence of the substance on the speed of light, independent of the volume which that substance occupies.

Several such formulæ have been proposed. First of all Newton, from his emissive theory of light, gave the expression $(n^2-1)\phi$, where ϕ is the specific volume (or the equivalent one $\frac{n^2-1}{d}$, where d is the density). This formula lost all theoretical basis on the victory of the undulatory theory. That it was, moreover, empirically untenable was proved by Gladstone and Dalė (1858), who also showed at the same time that the similarly formed but simpler function $(n-1)\phi$ or $\frac{n-1}{d}$ remained much more constant with the temperature, and was therefore to be considered the real measure of the refractive power.

When this formula was tested by Landolt and others, it proved not to give quite constant values, although the approximation was tolerably good. No theoretical foundation for it was proposed.

In the attempt to find a theoretically deduced formula, even though the basis was partly hypothetical, L. Lorenz and H. Lorentz (1880) put forward the same expression $(n^2-1)/(n^2+2)d = \text{constant}$. Since the one was deduced from the assumptions of the elastic ether theory of light, and the other from the electromagnetic theory of light, the agreement of the two lines of development lent an air of probability to the view that the result was of more general significance than either of the fundamental assumptions could confer.

The significance of such formulæ is that they represent the influence of the substance on the speed of light, dependent only on the nature of the substance and not at all on its arbitrarily variable conditions. The formulæ are tested by bringing a given substance into as many different conditions as possible, and observing whether the formula changes its value or not.

These different conditions can be obtained in several ways. The temperature or the pressure may be changed, and thus the density altered, or the substance may be dissolved in another of known refractive power, and it is observed whether the value of the expression is additively made up of the values of the components.

In the first two methods, all that has to be done is to determine the density d at the variable temperature or pressure, along with the corresponding refractive index, put them into the formulæ, and compare the results.

The method of mixture depends on the following rule: If r_1 and r_2 are the values of any function of the components, and r that of the mixture in which the amounts of the two components are x and 1 – x, the additive relation is $r = xr_1 + (1 - x)r_2$.

When the three formulæ $(n^2 - 1)/d$, $(n - 1)/d$, and $(n^2 - 1)/(n^2 + 2)d$ are put to the test, none of them completely satisfies the condition of independence of the external conditions. The first formula is the worst in this respect, and has been generally discarded on this account. The other two are practically equally good, first the one and then the other being in better agreement with the facts. The simpler one would be preferred but for the fact that the last formula (apart from its not very convincing theoretical development) is markedly superior in one particular instance. While the other formula is inapplicable in the comparison of the refractive index of volatile substances in the liquid and gaseous states, Lorenz showed that the last formula holds in a large number of instances, notwithstanding the enormous change of density. The following table gives the values of $(n^2 - 1)/(n^2 + 2)d$ for the two states :—

	Liquid (20°).	Gas.
Ethyl ether	·3029	·3068
Ethyl alcohol . . .	·2807	·2825
Water	·2061	·2068
Chloroform	·1791	·1796

For this reason the third formula is the only one in use at the present time. It is of little importance for our present purpose which is used, as the general relations are exhibited in the same form by both, only with different numerical values.

Before we enter upon these relations, it must be noticed that the refractive constant varies with the wave length of the light. The refractive index is usually greater the smaller the wave length, and to a different extent for different substances; or, in other words, the dispersion is different for different substances. If it was proportional to the refractive index, as Newton had assumed, this influence would be eliminated by referring all the values to any given wave length, the change to any other wave length being effected by means of a constant factor. No such simple relation exists, and the question has been much discussed how to get over the difficulties. Schrauf (1862) proposed to use, instead of any definite wave length, the constant A of the dispersion formula of Cauchy $n = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} + \ . \ . \ .$, where λ is the wave length, and in which for $\lambda = \infty$ the index of refraction $n = A$, and the proposal was in many cases accepted. It seemed, indeed, rational to reckon with the index of refraction for infinitely long waves instead of that for any definite wave length. But it turned out that the formula by no means satisfactorily represented the dispersion; according to the observations employed, different values were obtained for A, and it has been made probable, particularly by measurements in the infra-red spectrum, that there is no limiting value of the index of refraction towards which it converges. The employment of a definite ray has therefore again come into practice, the values being mostly made referable to the red hydrogen line of wave length 656·2 millionths of a millimetre, or to the sodium line, which coincides with the D line of the solar spectrum.

For stoichiometric purposes, the refractive index referred to unit mass (by means of the density) is multiplied by the molar weight m; the values thus obtained are referred to chemically comparable quantities. This molar refraction is

$$R = m(n-1)/d, \text{ or } R = m(n^2-1)/(n^2+2)d,$$

and the first question that arises is as to the molar refractions of chemically comparable substances, and, in particular, to the connexion between the values for compounds and for the elements contained in them.

Berthelot (1856), using the erroneous formula of Newton, first approached this question, and showed that it is really an additive property. In a very comprehensive and careful investigation Landolt (1864) applied Gladstone's formula, and found that, for certain classes of substances, the additive property is fully established.

The procedure was precisely the same as that followed by Kopp in the investigation of molar volumes. First it was shown that equal differences in chemical composition correspond to equal differences in the molar refraction; then atomic refractions were calculated for the elements, the sum of which, after each had been multiplied by the atomic coefficient, should give the molar refraction. If R is the molar refraction of a compound, the elements of which have the atomic refraction $R_1, R_2, R_3, \ldots$, and the number of each kind of atom in the compound is $n_1, n_2, n_3, \ldots$, the formula is

$$R = n_1R_1 + n_2R_2 + n_3R_3 + \ldots$$

In this manner Landolt investigated many organic substances in the fatty series, with the result that the formula is in tolerably good, but not in absolute agreement with the experimental facts. Effects similar to those observed by Kopp in the case of the different oxygen linkings, were clearly recognisable, but were not followed further.

Using Gladstone's formula, Landolt calculated the atomic refractions C = 5·00, H = 1·30, O = 3·00. An example will illustrate their use. For ethyl alcohol, C_2H_6O, $d = 0·8011$, $n = 1·361$. As $m = 46$, $m(n-1)/d = 20·70$, while the sum of the atomic refractions is 20·80. The agreement is within ·5 per cent.

Although the additive regularity was the prominent feature of this earlier work, it was quite apparent that it was not the only effect. Gladstone and Landolt had pointed out individual exceptions; afterwards Brühl (1880) discovered a constitutive influence, the double linkage of carbon always producing large and regular deviations from the original scheme. Substances containing it always possess a greater molar refraction than that calculated from the atoms, and thus the law of Landolt has to be extended in the same way as Kopp's law for molar volumes. Together with the additive summation we have the constitutive influence, so that the elements contribute differently to the molar refraction according to the function which they exercise in their compounds.

This was first investigated in detail for carbon, but other measurements show that it holds for other elements, and not merely for those like oxygen, sulphur, nitrogen, etc., which have variable valency and modes of combination, but also for univalent elements. The following table is given by Brühl:—

Carbon	2·48
Hydrogen	1·04
Hydroxyl oxygen	1·58
Carbonyl oxygen	2·34
Chlorine	6·02
Bromine	8·95
Iodine	13·99
Nitrogen (single bond)	3·02
Double linking of carbon	1·78
Triple linking of carbon	2·18

The two last values signify that two double-linked carbon atoms do not possess the atomic refraction $2 \times 2{\cdot}48 = 4{\cdot}96$, but rather $4{\cdot}96 + 1{\cdot}78 = 6{\cdot}74$; in the same way two triple-linked carbon atoms have the refraction equivalent $4{\cdot}96 + 2{\cdot}18 = 7{\cdot}14$.

With the help of these constants (which are given with reference to the formula $\frac{n^2 - 1}{n^2 + 2} \cdot \frac{m}{d}$ and the α hydrogen line) we get molar refractions of compounds which agree very well with those observed. The considerable and very constant influence of double linking has frequently proved to be of use in the discussion of questions of constitution.

We should not assume that the differences between measurement and calculation which still remain are due entirely to errors of observation. In fact it appears from the very extensive material now accumulated that such differences have an actual existence. They are caused in part by our present inability to take dispersion into account, substances with strong dispersion yielding quite regularly a greater molar refraction than that calculated from the preceding constants. But substances also which have no great dispersive power exhibit similar small deviations, so that the conclusion we already came to, that constitutive influences are always effecting slight alterations on the additive scheme of the refractive constants, holds in the most general manner. The determination of the nature and amount of these influences still remains the task of the future.

The above constants may be partly tested by calculating the atomic refractions of the free elements from their refractive indices and densities. Thus from the values for gaseous hydrogen and chlorine we get the refraction $H = 1{\cdot}05$ and $Cl = 5{\cdot}78$, which agree very well with those obtained from the compounds.

In other cases, again, the deviations are large, even in the calculation of the molar refraction of the simplest compounds. The position here is the same as in the case of the molar volume (p. 226). The constitutive influence is most clearly shown in the first members of the different series of comparable substances, and it is erroneous to draw conclusions regarding the constitutive properties of simple compounds from the behaviour of more complex substances. They require individual treatment.

This applies more particularly to the refraction coefficients of gaseous substances. Although we know no state which is so comparable as the gas state, the refractive indices of gases are absolutely at variance with the additive scheme. The reason is that they are, as a rule, quite simple compounds, and their individual characteristics predominate. The refraction of the vapours of more complex substances reproduces the regularities observed in liquids.

The inorganic compounds have been much less thoroughly investigated than the organic. We owe almost all we know of this subject to the work of Gladstone. Here also we find a general additive law, though it is distinctly modified by constitutive influences. For instance, the molar refraction of free acids differs from that of their potassium salts by numbers which are very nearly equal in the case of all strong acids; and this, likewise, is the case for weak acids, the differences in the two groups being, however, unequal. Similarly, when a metal can form several series of salts it appears to have a different atomic refraction in each series.

The determinations of the refractive power of such substances are in general performed on their aqueous solutions. If these consist of p mols of water to one mol of salt, then we have the relation (p. 229)

$$(18{\cdot}01p + m)r = 18{\cdot}01pr_0 + mR,$$

where 18·01 is the molar weight of water, m that of the salt; r, r_0, and R the refractive constants $\left(\text{either } (n-1)/d \text{ or } \frac{n^2-1}{n^2+2}\frac{1}{d}\right)$ of the solution, the water, and the salt. For the molar refraction of the salt we thus have

$$mR = (18{\cdot}01p + m)r - 18{\cdot}01pr_0.$$

By special experiments Gladstone convinced himself that, whether the molar refraction is determined from the solid salt (he used prisms of rock salt) or from solutions, the result is the same, but later investigations have shown this to be inexact.

Boiling-Points.—The first regularity connecting the properties of substances with the chemical composition was observed in the boiling-points of organic compounds. In the remarkable development of organic chemistry during the early half of the nineteenth century the boiling-point was employed as an important characteristic of newly discovered substances, and a fairly large mass of data was available. H. Kopp (1842) stated that equal differences of chemical composition in organic compounds correspond to equal differences of their boiling-points. Every ethyl ester of an acid, for example, boils 19° higher than the corresponding methyl ester, and the acid itself 45° higher than the ethyl ester.

This indicates an additive property, since the corresponding differences are constant. But while Kopp, with scientific caution, limited his rule to the comparatively narrow region of the known, some of his contemporaries attempted to apply the additive scheme in its widest form. These attempts all came to grief, and necessarily so, for temperatures are not additive quantities at all, being intensities (p. 31); their algebraic summation is therefore devoid of meaning.

Later research, then, has not brought us much further than Kopp's rule given above; indeed the application even of it has had in many cases to suffer restrictions. Metameric substances, for instance, ought by it to have the same boiling-point, but this is not exactly the case. It has been found rather that the differences in the constitution of isomeric compounds with similar chemical function (differences unknown to Kopp when he published his principle) always determine differences in the boiling-point. Examples of such bodies are to be found in the primary, secondary, and tertiary alcohols and acids; the so-called position-isomers amongst the benzene derivatives, etc. It is true that here also the differences are probably of a regular nature, the primary alcohols boiling higher than the secondary, and these again higher than the tertiary; or, in the other group, the para compounds usually higher than the ortho and meta compounds. These regularities, however, are of a somewhat limited character and admit of so many exceptions that they need only be indicated here.

Substances having the same composition but differing in properties are said to be different in constitution; the corresponding differences of properties may also be said to be constitutive. This difference is ordinarily ascribed to a different arrangement of the atoms contained in the substance. As this is a hypothetical representation, we may seek to express the facts without recourse to any hypothesis. It is found in the circumstance that, without exception, substances of identical composition and different properties possess different amounts of energy, and therefore behave differently when they suffer any change, whether alone or in conjunction with other substances. It is as well, therefore, to connect together the idea of constitution and the quantity of energy; still, for the sake of brevity, use may be made of the elaborated formal language in which the chemistry of the time expresses it. For the only significance of structural and spatial formulæ is that they provide an intelligible representation of chemical changes and reactions.

As has been seen already, additive and constitutive properties are so connected that the properties are additive if the substances are chemically similar, and the additive property disappears when the substances compared are not so closely related. In particular, isomeric substances are more nearly alike in properties the more nearly alike their constitutions. In other words, the numerical values of the physical properties are parallel to their chemical relationship.

Although it is as yet impossible to assign numerical values to such chemical similarities, the rule has been frequently applied with advantage. Particularly in doubtful cases it is of use in ascertaining chemical similarity, and in this respect the stoichiometry of constitutive properties (a large number of which exist) has become highly important.

To give a few examples, by way of illustration, the boiling-points of the isomeric esters of fatty acids are not the same: they are pretty near, however, and are nearer the smaller the difference in the isomeric acid or alkyl group. The boiling-points of the fatty acids which are isomeric with these esters, are higher still, but similar relations again hold. The following table makes this clear :—

Isomeric Esters, $C_5H_{10}O_2$.		Isomeric Acids, $C_5H_{10}O_2$.	
methyl n-butyrate	102·3°	n-valeric acid	186·4°
methyl i-butyrate	92·3°	i-valeric acid	176·3°
ethyl propionate	98·8°	trimethylacetic acid	163·8°
n-propyl acetate	100·8°	ethylmethylacetic acid	177·0°
i-propyl acetate	91·0°		
n-butyl formate	106·9°		
i-butyl formate	97·9°		

Rotation of the Plane of Polarisation.—The ability of certain liquid substance to rotate the plane of polarisation of light is of an entirely constitutive character. It is a property possessed by relatively few bodies, which are all, so far as we know, compounds of carbon, and in these it occurs only in connexion with certain quite definite circumstances, as we shall see below.

The angle through which the plane of polarisation is rotated by liquids is dependent on their nature as well as on the wave length of the polarised light. It is proportional to the thickness of the layer of liquid passed through, and varies with the temperature.

The angle through which polarised light of definite wave length is turned when it passes through a layer whose thickness is inversely proportional to the specific gravity of the liquid is called the specific rotatory power of that liquid. It is denoted by $[\alpha]$ and we have the relation

$$[\alpha] = \frac{\alpha}{\mathrm{ld}},$$

where α is the observed angle, l the thickness of the layer, and d the density of the liquid. The decimetre is usually employed as the unit of length.

If we multiply this value by the molar weight m, then $m[\alpha]$ represents the molar rotation. As the numbers are very large, the hundredth part of this value is usually taken,[1] so that the molar rotation $[\mathrm{m}] = \frac{\mathrm{m}\alpha}{100\mathrm{ld}}$.

The determination of the rotatory power is mostly made for one definite kind of light, almost without exception for the yellow light of the sodium flame; the corresponding values are denoted by $[\alpha]_D$ and $[\mathrm{m}]_D$, the sodium line corresponding to the D line in the solar spectrum.

The general laws governing these phenomena were first made out by Pasteur (1848) in an investigation of the different tartaric acids. In addition to ordinary dextro-rotatory tartaric acid, racemic acid has been known for a long time; it has the same composition, but has different properties, and it does not rotate the plane of polarisation. Pasteur discovered that it can be split up into two different acids, the one identical with ordinary dextro-tartaric acid, the other the same in every chemical and physical property, except that it is lævo-rotatory.[2] When equal amounts of the dextro- and lævo-acids in solution are mixed, the resulting solution has all the properties of a solution of racemic acid.

There is thus an "optically symmetrical" isomer of ordinary dextro-tartaric acid with exactly the same properties, except for the opposite sign of rotation, which can form with it an inactive compound with different properties. It follows from the inactivity that the two active acids are optically perfectly symmetrical, since otherwise they could not exactly compensate each other. This is confirmed by direct observation.

Subsequent research by Pasteur and his successors on other substances proved this to be a general relation; all optically active substances occur in pairs, one dextro, the other lævo. These can

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[1] If the length is given in cm. the molar rotation would be of convenient size without the factor 100.

[2] Crystals of the two acids also exhibit "dextro" and "lævo" forms.

form inactive compounds, which are named racemic from the original case.

The chemical property which causes the optical activity must be connected with the symmetrical character, in order that it can operate in two equal and opposite ways.

Pasteur further showed that the immediate derivatives of an optically active substance (such as salts of the acids) are also active; as are also some of the more distant derivatives, although certain changes destroy the activity. This leads to the conclusion that the rotatory power is connected with a definite complex in these compounds, and this may be found by observing the appearance or disappearance of the activity.

The Asymmetric Carbon Atom.—Now Le Bel and van't Hoff showed almost simultaneously (1874) that all optically active substances which could rotate the plane of polarisation in the non-crystalline state contained an "asymmetric" carbon atom, *i.e.* one whose four valencies were satisfied by four atoms or radicals of different kinds.

The causal connexion between optical activity and the asymmetric carbon atom can be proved in two ways.

If the asymmetric carbon atom is the cause of the activity, every active substance must contain one, and every substance containing one must be optically active.

The first of these conclusions is very easily verified. With the exception of a few doubtful cases, which were soon cleared up in a satisfactory manner, in all known active substances the constitution either already contained an asymmetric carbon atom, assigned on purely chemical grounds, or it could be assumed without contradicting the other known facts. From this point of view the theory was eminently satisfactory.

It did not appear to fulfil the other condition so satisfactorily, for very many substances were known, which were supposed on chemical grounds to have an asymmetric carbon atom, and were, nevertheless, optically inactive.

The symmetry relation discovered by Pasteur affords an explanation of this, and is at the same time a new postulate. It must be assumed in all these cases that an inactive compound with an asymmetric carbon atom is the racemic form, and the problem is to separate it into its active components. Experiments directed to that end have proved in very many cases the possibility of effecting this separation. The theory is thus confirmed in this direction.

The methods of separation depend on two quite different circumstances. All the compounds of symmetrical active substances with an inactive constituent are identical, but not those formed with another active constituent. Thus the salts of dextro- and lævo-tartaric acid have the same properties if the hydrogen is replaced by metals; if salts of optically active alkaloids are prepared, the salt of the dextro-acid is not only optically different from that of the lævo-acid, but differs in solubility, water of crystallisation, etc. They can be separated by the ordinary process of fractional crystallisation, and so the separation of the acids is effected.

The second process depends upon the fact that at certain temperatures, which must be ascertained for each case, solutions of racemic compounds deposit separate crystals of the active components. Although all the physical properties of the crystals—such as colour, density, habit—are the same, the crystal forms are usually symmetrically different. While all the crystal angles are the same, the arrangement of certain faces is symmetrically opposite, the crystals being in the relation of object and mirror image, or of right and left hand. When crystallisation occurs in this manner, the two forms can be separated by picking out the dextro- and lævo-crystals.

A third process, depending upon the living activity of fungi or bacteria which consume one of the two forms more rapidly or exclusively, is probably to be included under the first method, since living protoplasm is optically active, and must act differently towards the two forms in the process of assimilation.

The Tetrahedron Hypothesis.—Van't Hoff and Le Bel have propounded in very similar terms a hypothesis to demonstrate the connexion between rotation and the asymmetric carbon atom. It represents the facts in a very convenient and illustrative manner. They assume that the four different radicals united with a carbon atom are arranged around it as at the apices of a tetrahedron. So long as two of the radicals are the same, the four can only be arranged at the apices in one manner, *i.e.* however they are arranged two such tetrahedra can be superposed by simple rotation. But when all four are different, there are two arrangements, and two only; they are not superposable, and are in the relation of object and mirror image. If these four radicals be denoted by a, b, c, d, and if the tetrahedra be imagined resting with one face on the plane of the paper, we have the following symmetrical but not superposable figures:—

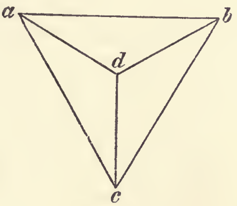


Fig. 33.

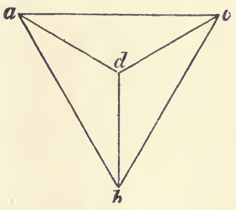


Fig. 34.

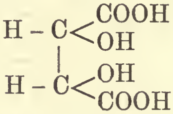
If the two tetrahedra are so placed that the radical d is at the apex, the order abc is in one case clockwise, in the other counter-clockwise.

Thus the two essential features of optically active substance find expression: the connexion with the asymmetric carbon atom, and the occurrence of optically active substances in a pair of symmetrical forms. The hypothesis, therefore, is both appropriate and useful.

Other circumstances, some of which were previously known, others first looked for and found as consequences of the hypothesis, are also simply and clearly represented by it; it has thus proved a valuable aid to further investigation of the subject.

The fourth form of tartaric acid affords a good example. Along with the two active tartaric acids and racemic acid there exists a fourth acid of the same composition which is optically inactive like racemic acid, but cannot like this be split up into the dextro- and lævo-acids. It also possesses different chemical properties from racemic acid.

To interpret this fact from the standpoint of the theory we must remember that tartaric acid, corresponding to the formula



$$\begin{array}{l} H-C{<}^{COOH}_{OH} \\ \quad\; | \\ H-C{<}^{OH}_{COOH} \end{array}$$

has two perfectly similar asymmetric carbon atoms. These may be so constituted that the ray of light is rotated by both in the same sense, either clockwise or the opposite; this would be the constitution of dextro- or lævo-tartaric acids. But, on the other hand, there may be united with each other two asymmetric carbon atoms with opposite action on the polarised ray. Then, as the constitution of the two asymmetric groups is in this case symmetrical, there will be complete compensation within the molecule itself—the substance is optically inactive and cannot be split up into active components.

The pronounced constitutive character of optical rotation precludes the possibility of extensive additive relations. Still additive characteristics may occur within narrow groups of comparable substances, just as has been observed in the case of boiling-points.

Investigation has shown the state of affairs here to be very different. Ascending a homologous series does not cause equal changes of rotation, which changes in a particular manner if a long series is considered; it first increases in one direction, reaches a maximum, and then slowly decreases. This is illustrated by the following measurements by Frankland on the esters of glyceric acid:

	Molar Rotation
methyl glycerate	− 5·76
ethyl ,, ...	− 12·31
propyl ,, ...	− 19·16
n-butyl ,, ...	− 17·85

If only a small number of members in a series are known, the change often appears to run in one direction; the general law here indicated has not been completely established in this simple form.

The behaviour of salts in dilute aqueous solution is very simply explained. The constitutive property of molar rotation is purely additive; *e.g.* salts of an active acid with inactive bases have the same rotation. The explanation is that the properties of dilute salt solutions consists of the sum of the properties of the ions, because of the electrolytic dissociation (p. 192).

In addition to active compounds containing the asymmetric carbon atom, active compounds containing asymmetric nitrogen, sulphur, selenium and tin are known. They all contain organic radicals.

Magnetic Rotation.—A group of phenomena closely related to the preceding is the magnetic rotation of the plane of polarisation, discovered by Faraday in 1846. Transparent substances brought into a magnetic field or into the interior of a coil of wire conducting an electric current, acquire the power of rotating the plane of polarised light, and retain this as long as the magnetic action lasts. The angle of rotation is proportional to the intensity of the magnetic field, to the thickness of the layer of substance through which the light has to pass, and is further dependent on the nature of the substance and the temperature.

The investigation of this subject was first carried out from the physical standpoint. Perkin (1882), to whom we owe almost all our knowledge of it, first considered the matter with reference to chemical composition.

The ratio of the rotations effected in the same magnetic field by the substance in question and by water he calls the specific rotation, the lengths of the two columns of liquid being inversely proportional to their densities. If ω be the angle of rotation for a column of the length l of the substance whose density is d, and if ω_0, l_0, and d_0 be the corresponding numbers for water at the same temperature, then the specific rotation $r = \frac{\omega l_0 d_0}{\omega_0 l d}$. The molar rotation is the ratio of the rotations of molar quantities and is

$$\rho = \frac{M\omega l_0 d_0}{18{\cdot}01\omega_0 l d} = \frac{M}{18{\cdot}01} r,$$

where M is the molar weight of the substance, 18·01 being that of water. The molar rotation of water is consequently equal to unity.

From a comparison of the molar rotations of different substances, an additive character in this property was only seen in homologous series; every addition of CH_2 in such corresponds to an increase of 1·023 units. This value remains the same for all series. The molar rotation can thus be represented by $C + 1{\cdot}023n$, where n is the number of CH_2-groups and C is a constant having a special value for each homologous series. These constants are purely constitutive; they are different for normal and iso-hydrocarbons, normal and iso-alcohols and acids. The formulæ, too, only hold for such compounds as possess at least one methylene, CH_2; for instance, the constant ·393 of the normal fatty acids does not apply to formic acid, $HCOOH$ and acetic acid, $CH_3.COOH$, in which CH_2 is not contained.

The magnetic rotation has, in virtue of these relations, repeatedly proved of use in determining to which of certain groups a newly discovered substance belongs.

These simple relations are not found among the more complex compounds of the aromatic series or in other cyclic compounds. The constitutive influence predominates to such an extent that little remains of the additive foundation. In this respect the magnetic rotation comes in between the molar volumes and molar refractions, on the one hand, and the boiling-points on the other. It is more affected by constitutive influences than the former, and less than the latter property. No systematic comparison from this point of view has been made as yet; noteworthy contributions towards it have been made by Perkin (1896).

BOOK III

CHEMICAL THERMODYNAMICS

CHAPTER X

THERMOCHEMISTRY

Introduction.—So far our considerations have been limited by the condition that the substances underwent no change in their chemical nature. We have now to inquire into the processes by which single substances change into others, or several interact with the production of new substances. In other words, chemical processes (in the strict sense) will now engage our attention.[1]

If we seek out the most general characteristic of natural processes, we find that all of them are connected with a time or space change in energy. No process occurs without such a change: if no change of energy takes place, we are not entitled to assert that any change has occurred at all.

All physico-chemical processes could be defined in terms of the kind and extent of the energy change which accompanied it. To do this would not only always be possible, it would be exhaustive. For all the modes of recognition we have for the various things of the outer world are related to their energy, since they consist essentially of processes which these things give rise to, directly or indirectly, in our sense organs, the latter only responding to the accession or withdrawal of energy. Thus all we know of the outer world are energy relations, and it may well be described as a system in which different kinds of energy are arranged in a definite manner in time and space.

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[1] Changes of state are to be regarded as chemical processes (in the wider sense). They were considered along with the static specific properties because of their real practical importance as characteristics of single substances. As is well known, boiling-points and freezing-points are largely made use of in the recognition and detection of substances, especially in organic chemistry.

This point of view also includes the phenomena with which chemistry is more especially concerned. No chemical process can occur without some change in energy, and a chemical process is fully defined if the amount of each kind of energy concerned is specified.

Energy relations are not only characteristic of the states of matter and of changes of state, they also contain the conditions for the possibility and the kind of change, which can take place under any given circumstances. In other words, all the known general and special laws of chemistry and physics can be reduced to one form, in which the processes governed by these laws appear as transformations or general relations of energy. These sciences are to be regarded as the science of energy or of Energetics—and the reduction to this form is the most general and exact which can at present be given to our knowledge.

Energy occupies this unique position in virtue of the general laws of the transformation of energy, which apply in all individual branches, and at the same time form a connecting link between them.

Energy and Matter.—Energy is frequently placed before matter, or at the least alongside of it, and the two regarded as the fundamental constituent of physical phenomena. The conception of matter is too indefinite for it to occupy this position. At best, matter is definable only by the kinds of energy, which coexist within certain limits of space. A stone is called material, because it has weight and mass, *i.e.* gravitational energy, and the power of taking up kinetic energy; its other properties, such as temperature, colour, chemical composition, describe its behaviour as regards heat, radiant energy, and chemical energy. The law of the "conservation of matter," which is usually placed alongside the law of "conservation of energy," does not apply to all these properties, but only to its mass, its relative weight, and its elementary chemical nature, while all other properties suffer change as the result of chemical action. The law is to be regarded as a special case of a more general law of energy. The only characteristic feature left is that all these kinds of energy are found together in the same space, and can be simultaneously moved together. This is the only fact which can be considered to be characteristic of a thing to which the name matter is applied; it cannot be claimed that this is in any way independent of our notion of energy.

The question has often been raised, What then is energy? A complete definition is given only by a description of its relations, and this is the content of all exact natural science. Taking into account the considerations previously discussed (p. 18), we may say energy is work, and everything which can be obtained from work and can be reconverted into work. It is thus characterised as the recognisable differences in time and space.

The importance of energy for the classification of experimental facts, apart from its general applicability in every region of physical phenomena, is that a number of general laws relate to energy, and that these apply in the same manner to every branch, enabling us to place known facts in clearer perspective, and to take in unknown ones. The relations between chemical energy and the other forms of energy must be preceded by an introduction on the general laws of energy, or on energetics.

The Kinds of Energy.—The kinds of energy known at the present time are divided into two groups, mechanical and non-mechanical. They are:

A. Mechanical—

1. Volume energy.
2. Surface energy.
3. Distance energy.
4. Form energy.
5. Kinetic energy.

B. Non-mechanical—

6. Heat.
7. Magnetic and electrical energy.
8. Chemical energy.

Light, or radiant energy in general, can no longer be regarded as a separate kind of energy, as the proof is practically complete that it consists of electromagnetic oscillations, similar to the oscillatory phenomena of sound produced by kinetic energy and volume or elastic energy.

The question whether the above are the only possible forms of energy, has not been raised. By combining all the imaginable variations possible in the case of so universal a thing as energy, we can represent the properties of other forms of energy which are conceivable, but are still unknown. It seems probable, from a preliminary investigation I have made, that there is a fairly large number of forms of energy still unknown.

The Factors of Energy.—**Intensity.**—Volume energy has been already dealt with in connexion with the gas laws (p. 30), which are an expression of the behaviour of this form of energy in the most important cases known to us. The amount of this energy, as previously shown, is measured by the product of two magnitudes—pressure and volume. This occurrence of two factors is general: all forms of energy can be split into two factors, the product of which gives the numerical value of the energy.

Each of these factors has special characters. The one is the expression of the presence or absence of a steady state or equilibrium between two neighbouring spaces, in which this kind of energy is present. In the present case pressure plays this part, two gases at the same pressure have no influence on the volume of each other, *i.e.* they are in equilibrium as regards volume energy. To ascertain whether the gases are at the same pressure, an apparatus, which indicates the presence and the difference of pressure, a manometer, is applied to each of them. If the indication on the manometer is the same when applied to each separately, we find the pressure is the same when the two gases are brought into direct contact. Consequently, if each of two pressures is equal to a third pressure, they are equal to one another; this is a rule which holds for all similar magnitudes, and is of great importance in spite of its apparently "self-evident" character (*cf.* p. 31).

Values which, like this, define the equilibrium of any form of energy, are known as strengths, or intensities (Helm, 1887); every form of energy has its intensity, a knowledge of which is essential for estimating its behaviour under any given conditions.

The instruments for measuring intensities deserve a few words; the account given of the manometer or pressure measurer can be applied appropriately to all measurers of intensity. A manometer can take up volume energy, and renders visible in some way the amount taken up. The manometer usually attached to steam boilers consists of a tube of elastic metal, which is expanded by the pressure exerted on its interior, until the elastic counter-pressure is in equilibrium with the applied pressure. This change of volume is easily read by means of a lever, which mechanically magnifies the small movements of the walls. The manometer cannot act, unless its volume is actually altered by the pressure; a perfectly rigid tube would be useless. But the amount of change is a matter of choice, and need only be very small if it is efficiently transmitted to the indicator. This is attained by reducing the weight and friction of the indicator. An instrument of this kind must always remove a certain amount of energy from the system whose intensity is being measured; but this can be made smaller, the less energy the "indicator" (in the widest sense) requires to actuate it. Still, it never can be reduced to zero.

This outline contains a general theory of instruments for measuring intensities, but it cannot be further developed here.

Capacity.—The other factor of volume energy is the volume. It does not obviously determine equilibrium, for any arbitrary volumes of gases may be in equilibrium. On the other hand, the transformation of volume energy into other forms depends on it, as it cannot take place without change of volume. Further, volumes are additive, and therefore quantities in the strict sense, since two equal volumes together give double the volume. Such quantities are called capacities.

An important property of capacities is expressed by the law of conservation which they follow.[1] This seems so self-evident as regards volume, because of our familiarity with the facts, that we have to remind ourselves of its existence, and cannot imagine it otherwise. There are, however, other capacities, with which we are less conversant, and the discovery of the special law regarding them marked a real advance.

The law states that the sum of the capacities in a given system remains constant throughout any possible change. When it is applied to volume energy, we see that the total volume cannot change, or that, if the volume of any one object is made larger, some other (or others) must decrease in volume to the same extent. That this is not "self-evident" is at once seen if an attempt is made to frame a similar rule for pressure; it will be found to fail. On the contrary, this property plays an important part in the description of the idea of space.

The next forms of energy, surface energy, distance energy and form energy, give rise to very similar considerations. The intensity factor of the first is the tension, its capacity factor is the surface; for the others they are distance and force, or more complex functions of space. There is no need to enlarge upon their properties as their transformation into chemical energy practically does not enter into the question.

The fifth form of mechanical energy is important in many ways. Its factors are mass and square of the velocity, according to the formula $\frac{1}{2}mv^2$ (p. 16). The mass is the capacity, the velocity is the intensity. For only when they have the same velocity (in magnitude and direction), so that they remain at the same distance apart, are two masses unable to affect the kinetic energy of each other.

The law of conservation of capacities here takes the form of the important law of the conservation of mass, which we came across at the beginning of our considerations, and is here seen to be a special case of the general law.

Kinetic energy may be analysed into two other factors, $\frac{1}{2}v$ and mv. The capacity is mv, and the law of conservation holds for this expression, known in mechanics as momentum. The form varies with the circumstances; it is best known as the law of conservation of the centre of gravity. As chemical relations are wanting, further detail is unnecessary.

Chemical Energy.—Although a description of the properties of the other forms of energy is relegated to the later portions of the

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[1] The law of the conservation of capacities is not absolute. The capacity for heat, the entropy, undergoes constant increase during all natural processes, and the pheuomena of radiation afford instances in which the law of the conservation of mass and of motion are infringed. The law is clearly a special case of a more general law, just as the law of the conservation of mechanical work is a special and limiting case of the law of the conservation of energy.

book, a few words may be devoted here to chemical energy. In general the total energy changes when one substance changes into others; this is ascribed to a changed content of the system in chemical energy, so far as other kinds of energy have not entered or left the system. The capacity and intensity factors must be sought for this kind of energy.

The capacity factor is the quantity of substance, which is proportional to the chemical energy, and its amount has no influence on any given chemical equilibrium. It must not be confused with mass or weight; it is proportional to both, but is not identical with either. This is apparent from the fact that two objects may be equal in mass and weight, and yet differ widely in respect to chemical energy. The law of conservation for this chemical capacity is not restricted to the conservation of the mass and weight in any given chemical change, but includes as a further special condition, the law of the conservation of the elements in chemical processes already mentioned (p. 111).

The capacity for chemical energy differs in one important respect from the others, and this difference is reflected in the intensity. Two masses or volumes differ only in numerical value, and are always positive. Two quantities of substances differ in kind as well as in numerical value. Consequently, while masses or volumes can be added or put together without limit, chemical quantities can only be added when they are alike in kind. Further, chemical capacities are subject to the relations expressed in the chemical equations which are founded on the laws of stoichiometry. This greater diversity of chemical energy adds much to the complexity of chemical energetics, and explains its tardy development.

New light is thrown on the question of the possibility of the transmutation of the elements. It cannot be said to be absolutely impossible, but it can be said that it is just about as probable or improbable as is a violation of the law of conservation of mass.[1]

The intensity factor of chemical energy has been named chemical potential, after the analogy of mechanical and electrical potential. It nearly coincides with what used to be vaguely called chemical affinity. It will be more clearly defined later. It will suffice for the present to state that equality of the chemical potential of the substances present is as essential for chemical equilibrium as is equality of pressure for the equilibrium of volume energy.

The doctrine of chemical affinity comprises the transformation of chemical energy into the other forms of energy, and there are as many divisions of the subject as there are forms. In the present state of science this programme is by no means complete, and our

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[1] Quite recently Ramsay has published experiments made with radium emanation, which point to the transmutation of the elements. On the other hand, according to the latest developments of the electron theory, mass appears to vary with the velocity.

knowledge of the various transformations has been developed to very different extents.

The divisions of the subject which have been longest recognised are Thermochemistry and Electrochemistry; the relation between radiant energy in the form of light and chemical energy, Photochemistry, is also a special division of the science. With regard to the four forms of energy, the relation of which to chemical energy should give rise to mechanochemistry, the connexion is indeed recognised, but has scarcely been mentioned in this direction. If we consider that in all chemical processes the concentration of the reacting substances changes, and that this has been proved to be necessary for the progress of the reaction, we recognise that volume energy is the form of energy which (partly in the form of osmotic volume energy, p. 171) changes place with chemical energy and conditions the phenomena. What was metaphorically called chemical mechanics, merits the name in the proper sense, since the doctrine of chemical equilibrium is actually the doctrine of the mutual relations between chemical energy and mechanical, particularly volume energy.

There still remains the relations between chemical phenomena and the other three forms of mechanical energy. They have been very little developed. It is known that the surface composition of solutions is different from that of the interior: here we have a relation between chemical and surface energy. Further, a few cases are known in which chemical processes were influenced by kinetic energy (the influence of centrifugal force on chemical equilibrium, Bredig, 1895), and a similar effect produced by gravity, a form of distance energy, has also been proved theoretically and experimentally. But these have not been developed to any extent, and they play a secondary part in natural phenomena and in technical processes, so that mechanochemistry is practically confined to the first-named relation to volume energy. It is only in very recent times that the significance of surface energy has been recognised.

Thermochemistry.—Chemical energy passes most easily and completely into heat. Thermochemistry, or the branch of science which treats of the relations between heat and chemical energy, is one of the oldest branches of affinity and is, at the present time, the most fully developed.

The importance of an exact knowledge of the amounts of chemical energy is at once apparent, when we consider the source and stores of energy necessary for important technical and physiological processes.

The sources of energy employed in the arts and manufactures are all of chemical origin, being referable to the combination of the elements of the fuel employed with the oxygen of the air. But, in addition to this, the vital activity of all organisms depends exclusively on chemical processes and the energy liberated through them. Chemical energy is consequently that form with which we have most extensively and frequently to deal, and which has the first and largest place in the economy of nature.

The history of thermochemistry begins accordingly with the technological and physiological problems propounded by Lavoisier and Laplace, Rumford, Dulong, Despretz, etc., who also attempted their solution. A theoretical foundation on one side is due to the first-named, who stated the principle that as much heat is required to decompose a compound as is liberated on its formation from the elements. This is a particular and very simple case of the general law of energy.

The Law of Constant Heat-Summation.—The law for thermochemical processes was first enunciated in its full extent by G. H. Hess (1840) as the law of constant heat-summation. He stated that the initial and final stages alone determine the development of heat in chemical processes; if these are specified, the development of heat is given, whatever may be the intermediate stages.[1]

According to our present notions a definite value of the energy of a system corresponds to each state it may assume, that which we call the "state" of the system being in fact fixed by the nature and quantity of the energy associated with the matter in the system. Two states, therefore, correspond to two quantities of energy, the difference of which must be conducted to or from the system if it is to pass from one state to the other. In how many stages this energy may be communicated has evidently no effect on the final value. But the form in which it is communicated will depend on the manner of transformation.

Hess established his principle as a conclusion from experiment, with full consciousness, however, of its wide import. He tested it in various ways, performing the same chemical reaction in different ways, and measuring the heat evolved in each process. The total was found to be the same however the single steps were varied. From his numbers the following table is selected :—

				Sum.
H_2SO_4	—	+ $2NH_3$ (in solution)	595·8	595·8
$H_2SO_4 + H_2O$	77·8	,,	518·9	596·7
$H_2SO_4 + 2H_2O$	116·7	,,	480·5	597·2
$H_2SO_4 + 5H_2O$	155·6	,,	446·5	601·8

The first column of figures represents the quantities of heat liberated by the action of one mol of sulphuric acid on one, two, and five mols of water; the second represents the quantities of heat evolved on the neutralisation of these diluted acids with ammonia. The sum of the corresponding members of both is approximately constant.

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[1] This law is only strictly true if all the processes take place at constant intensity of external energy (pressure, temperature). As a rule this condition is practically satisfied in thermochemical work.

The significance of this principle for the practice of thermochemistry is very great, and was fully appreciated by Hess. It enables us to calculate the heat-effect of processes which cannot be directly determined; for we may represent them as terms of a sum, of which the total value and the other terms are known. We cannot, for example, measure the heat given out on the combustion of carbon to carbon monoxide. If, however, we measure the heat evolved when carbon is oxidised to carbon dioxide, then this must be equal to the heat of combustion of carbon to monoxide plus that of monoxide to dioxide. The latter can also be directly ascertained, so that the difference of the two observed values gives the required heat of combustion of carbon to carbon monoxide.

Contemporaneously with Hess, who is to be looked upon as the real founder of thermochemistry, and after him, other investigators were busy at this subject, viz. Andrews, Graham, and especially Favre and Silbermann, who collected a rich store of observations. In clearness of ideas, however, these are all inferior to Hess.

The results of the mechanical theory of heat, which had meantime been developed, were first applied to thermochemistry by Julius Thomsen (1853). This chemist has up to recent times accumulated an enormous number of data, mostly determined with considerable accuracy. Berthelot in 1865 began to occupy himself with similar problems, more particularly in organic chemistry. It is to these two investigators that we owe the greatest part of our acquaintance with the domain of thermochemistry. A large number of very accurate determinations of heats of combustion has been made by F. Stohmann and W. Luginin.

Thermochemical Methods.—The calorie is the unit of heat hitherto used in thermochemistry, *i.e.* the quantity of heat required to warm one gram of water one degree. As already explained, this is not a rational unit, and ought to be replaced by the erg or a multiple of it. A very convenient unit for thermochemical purposes is the kilojoule (kj.), equal to 1000 joules or 10^{10} ergs. It will be adopted in this book. To recalculate into ordinary units, according to Rowland 1 cal. = 41,830,000 erg at 18°.[1]

To obtain calories from kilojoules, divide by ·004183, or multiply by 239·1. If mean calories K = 100 cal. are wanted, the factor is 2·391.

Thermochemical Equations.—In order to formulate the facts of thermochemistry shortly and in a form suitable for calculation, we shall extend the signification of the ordinary chemical equations in such a way that they will represent not only the mass-relations but also the energy-relations. For example, when we write the equation

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[1] As the mean of all determinations, the value 41,870,000 has been recently recommended. The difference, 1 in 1000, is so small that the older, well-known coefficient 41,830,000 may be retained, provisionally at least.

$$Pb + 2I = PbI_2,$$

this states that lead iodide is formed from lead and iodine, 207·1 g. lead and 253·9 g. iodine giving 461·0 g. lead iodide. If the formulæ are to represent, not the quantities of the substances but the quantities of energy associated with them, the equation is incomplete. For on the formation of lead iodide heat is liberated to the amount of 167 kj.; the energy of lead iodide is less than the energy of its components by this quantity. The corresponding equation for energy is therefore

$$Pb + 2I = PbI_2 + 167 \text{ kj.},$$

and signifies that 207·1 g. lead and 253·9 g. iodine together contain as much energy as 461·0 g. lead iodide plus 167 kj.

The equation may be algebraically transformed, but then its signification is somewhat different. Thus

$$Pb + 2I - PbI_2 = 167 \text{ kj.}$$

means that the difference of energy between lead plus iodine, and lead iodide amounts to 167 kj. Or

$$PbI_2 = Pb + 2I - 167 \text{ kj.}$$

represents that 167 kj. must be supplied when lead iodide is decomposed into lead and iodine.

All the equations are to be so understood that the energy of the substances only holds for one and the same temperature, usually the mean laboratory temperature of 18°.

The amount of energy in a substance is further dependent on its state of aggregation. It is simplest to indicate the state by means of brackets.[1] As liquids are most frequently under consideration they will be indicated without brackets. Gases will be indicated by round brackets, solids by square brackets. Then the equations

$$H_2O - [H_2O] = 6{\cdot}0 \text{ kj.}$$
$$(H_2O) - H_2O = 40{\cdot}5 \text{ kj.}$$

signify that on the transformation of water into ice 6·0 kj. are liberated, and on the transformation of water vapour into liquid water, 40·5 kj.

It may be observed, as we have till now tacitly assumed, that the quantities of energy and heat refer to mols, *i.e.* to such quantities of the substances as amount to their formula-weights in grams.

The reacting substances are very often dissolved in a large quantity of water. This is denoted by adding the letters Aq (aqua) to the ordinary chemical symbol. Such solutions when further

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[1] This suggestion was made to me by a colleague whose name I have forgotten.

diluted with water neither absorb nor evolve heat. Thus the equations

$$\mathrm{M.Aq} + n\mathrm{H_2O} = \mathrm{M.Aq}$$
$$\mathrm{M.Aq} - n\mathrm{H_2O} = \mathrm{M.Aq}$$

hold good, M being the dissolved substance. We may therefore in thermochemical equations add or subtract limited quantities of water when the substances are in solution without introducing any appreciable error.

For instance, we have for the formation of potassium chloride in aqueous solution

$$\mathrm{KOH\ Aq} + \mathrm{HCl\ Aq} = \mathrm{KCl(Aq + Aq + H_2O)} + 57{\cdot}3\ \mathrm{kj.}$$

Instead of this equation we always write

$$\mathrm{KOH\ Aq} + \mathrm{HCl\ Aq} = \mathrm{KCl\ Aq} + 57{\cdot}3\ \mathrm{kj.},$$

as the mixing of the liberated water with the solution of potassium chloride has no thermal effect whatever.

Indirect Determinations.—These energy-equations are specially useful in calculating thermochemical data which cannot be directly observed. If we return to the example given by Hess (p. 249), we have from direct measurement

$$[\mathrm{C}] + 2(\mathrm{O}) = (\mathrm{CO_2}) + 394\ \mathrm{kj.}$$
$$(\mathrm{CO}) + (\mathrm{O}) = (\mathrm{CO_2}) + 284\ \mathrm{kj.}$$

Subtracting the lower from the upper equation we get

$$[\mathrm{C}] + 2(\mathrm{O}) - (\mathrm{CO}) - (\mathrm{O}) = 110\ \mathrm{kj.}$$

or

$$[\mathrm{C}] + (\mathrm{O}) = (\mathrm{CO}) + 110\ \mathrm{kj.},$$

i.e. the heat of combination of carbon and oxygen to form carbon monoxide is 110 kj.

A second somewhat more complicated example is the heat of formation of sulphur trioxide, also determined by Hess. The process consisted in burning a mixture of lead oxide and sulphur in oxygen. Lead sulphate is formed with an evolution of 692 kj.; we have therefore the equation

$$[\mathrm{PbO}] + [\mathrm{S}] + 3(\mathrm{O}) = [\mathrm{PbSO_4}] + 692\ \mathrm{kj.}$$

To eliminate the terms PbO and $\mathrm{PbSO_4}$, lead oxide was transformed into lead sulphate by solution in dilute sulphuric acid; the result was

$$[\mathrm{PbO}] + \mathrm{H_2SO_4Aq} = [\mathrm{PbSO_4}] + \mathrm{Aq} + 97\ \mathrm{kj.}$$

Subtracting, we get

$$[\mathrm{S}] + 3(\mathrm{O}) + \mathrm{Aq} = \mathrm{H_2SO_4Aq} + 595\ \mathrm{kj.},$$

i.e. the formation of aqueous sulphuric acid from sulphur, oxygen, and water is accompanied by the evolution of 595 kj.

Lastly, Hess dissolved sulphur trioxide in water—

$$[SO_3] + Aq = H_2SO_4Aq + 172 \text{ kj.}$$

Subtracting again, we have as the final and desired result—

$$[S] + 3(O) = [SO_3] + 423 \text{ kj.}$$

In the same way a great many other problems may be solved. The method is to measure any two reactions in which the initial and final substances take part, and then to eliminate the subsidiary bodies by suitable equations between them. It depends upon the skill of the experimenter to so choose the reactions that the measurements may be as exact as possible, and that the end may be attained with the fewest possible intermediate stages.

Heat of Formation.—The heat of formation is a heat of reaction extremely often calculated. By this name we indicate the difference between the energy of a chemical compound and that of its component elements. The numbers are obtained from equations in which only the elements and the compound occur. It follows from

$$[Pb] + 2[I] = [PbI_2] + 167 \text{ kj.}$$

that the heat of formation of lead iodide is 167 kj.

This heat is, therefore, the loss of energy suffered by the elements when they unite to form the compound in question. If the quantities of energy, whose absolute magnitudes are quite unknown, be reckoned from the energy of the elements taken as zero, the equation assumes the form

$$0 + 0 = [PbI_2] + 167 \text{ kj.},$$

if we make $[Pb] = 0$ and $2[I] = 0$. This can also be written

$$[PbI_2] = -167 \text{ kj.}$$

Therefore, in the energy-equations the formulæ of the compounds may be replaced by their heats of formation with the signs changed.

In this way we can easily calculate heats of reaction by means of the heats of formation. Suppose we wish to find the heat given out in the preparation of magnesium from magnesium chloride and sodium. We have

$$[MgCl_2] + 2[Na] = 2[NaCl] + [Mg] + x.$$

Now the heat of formation of magnesium chloride is 632 kj., and of sodium chloride 408 kj. Making the substitution and putting the heats of formation of the elements equal to zero, we obtain

$$-632 + (2 \times 0) = (-2 \times 408) + 0 + x$$
$$x = 184 \text{ kj.}$$

On account of this simple form taken by the equations, it is usual to determine the heat of formation of the various chemical compounds, so that the values may be used in further calculations. Heats of formation are consequently given by preference in the tables contained in the following chapters.

Methods.—With respect now to the actual performance of thermochemical experiments, there are several general statements that may be made, in spite of the variety in the methods and apparatus employed by different investigators. Only a relatively small number of the numerous reactions known to experimental chemistry are suitable for thermochemical measurement, these being almost exclusively such as take place at ordinary temperatures and are at an end in the space of a few minutes. The chief among them are the phenomena of neutralisation, of solution, and of dilution.

A second class of thermochemical processes is formed by rapid combustions, which, by being conducted in a completely closed vessel surrounded by water, are likewise amenable to convenient measurement. The majority of thermochemical experiments may be reduced to one or other of these forms.

For thermochemical measurements in aqueous solution calorimeters constructed of glass or metal (platinum by preference) are used.

If the dissolving of a solid, liquid, or gas in the liquid of the calorimeter is in question, the experiment is so conducted that the substance is brought as nearly as possible to the temperature of the calorimeter and the process then initiated. The uniform distribution of the heat as well as of the reacting substances is provided for by an efficient stirring apparatus. This has usually the form of a horizontal plate, which contains suitable openings for the passage of a thermometer, etc., and has an up and down motion.

If the reaction is between two approximately equal quantities of liquid, the temperature of each must be accurately measured at the moment of mixing. Thomsen in this case arranges a smaller vessel on the top of his calorimeter, each vessel being provided with thermometer and stirrer, and after having read off the temperature of both, lets the liquid in the upper vessel flow through a valve in the bottom into the lower vessel. Berthelot introduces one of the liquids into his calorimeter, but then, unlike Thomsen, has the other in a thin-walled, wide-necked flask standing inside a protective copper cylinder with a silvered and polished interior. When the temperature has been ascertained, the thermometer serving as stirrer, the flask is seized by means of wooden tongs and its contents emptied into the calorimeter. He rejects Thomsen's arrangement because the liquid in flowing through the valve may possibly experience a change of temperature. This objection is unfounded, however, for by the way in which Thomsen makes his thermometers comparable, an error of this nature is eliminated. In reality, Thomsen's apparatus is the more exact, which is most likely owing to the fact that his thermometers are read off through a telescope, while Berthelot uses the naked eye.

The Combustion Calorimeter.—The calorimeter employed for the combustion of solid, liquid, and gaseous substances in gases has been gradually evolved from the imperfect instruments of Dalton, Davy, and Rumford, by the labours of Dulong, Despretz, and in particular of Favre and Silbermann. It consists of a cylinder filled with water into which the combustion-chamber is sunk; a number of tubes, destined to supply the necessary gases, open into it, and the products of combustion are led through a long spiral metal tube or worm, in order that all their excess of heat may be given up to the water of the calorimeter.

The apparatus has experienced but little change in the course of time. Thomsen makes the metallic parts of platinum, and Berthelot has introduced a glass combustion-chamber, which admits of very convenient observation of the progress of the reaction.

Of late years compressed oxygen has been substituted for oxygen at ordinary pressure, which is almost entirely superseded. The apparatus was elaborated by Berthelot and Vieille (1881); it consists of a stout-walled steel vessel, lined with platinum (or with enamel in the cheaper models). A screw valve admits the oxygen under pressure, usually of 25 atmospheres. The substance to be burned is suspended in a small platinum basin in the middle of the "bomb." Ignition is brought about by heating a thin iron wire to incandescence by means of an electric current, and the white-hot drops of iron oxide fall upon the substance.

Solids and non-volatile liquids are placed direct in the basin; volatile liquids are enclosed in little collodion sacs. Some substances rich in oxygen do not undergo complete combustion under these conditions; in such cases a known quantity of naphthalin is mixed with it, and a correction applied for its heat of combustion.

This method has the advantages that the process is instantaneous, and that combustion is complete. Most substances on combustion in oxygen at ordinary pressure yield some carbon monoxide as well as carbon dioxide, and it is difficult to apply an accurate correction for it.

Work with the bomb is much facilitated by the use of commercial oxygen at a pressure of 100 atmospheres, as recommended by Stohmann.

Another process is the combustion with combined oxygen (especially with potassium chlorate), first employed by Frankland (1866) and later improved and applied by Stohmann and his pupils. The substance is here mixed with potassium chlorate and some indifferent material (*e.g.* pumice), and made into a sort of firework, which is set off inside a water-calorimeter. It is no longer used. The substitution of sodium peroxide for the potassium chlorate has not added much to the reliability of the method.

It should be mentioned, in conclusion, that Bunsen's ice-calorimeter has been in some cases used for thermochemical experiments. Although this method gives very exact results, even with small quantities of substance, it requires excessively skilful manipulation, and the instrument must be set up in a cold place, the temperature of experiment being 0°. Working at this temperature is frequently an advantage, but in certain cases decidedly detrimental.

Measurement of the Temperature.—The measurement of temperature is at once the most important and the most difficult part of a calorimetric determination. It is true that very sensitive thermometers can be constructed by the employment of narrow capillaries and somewhat large bulbs, and as a rule we use such as are divided into $\frac{1}{50}$ degree, which therefore admit of the estimation of $\frac{1}{500}$ degree when read off with a telescope. The difficulty, however, lies less in the want of sensibility in the thermometers than in the continual heat-exchange of the calorimeter with the surrounding objects, the proper thermal results being more or less disturbed by this. The error is greater with a small calorimeter; with a calorimeter of 500 ccm. capacity we get the minimum error, the disturbance falling in this case within the limits of accuracy given by the measurement of temperature.

To diminish the radiation as much as possible the calorimeter is brightly polished, and placed within a cylinder also polished in the interior. Berthelot surrounds this last with a large jacket of tinplate filled with water; Thomsen prefers to employ cases of metal or cardboard, the intervening spaces merely containing air. A great improvement is effected by the use of vacuum mantles, *i.e.* double-walled vessels pumped out to a high vacuum. Heat convection by means of the warmed air is reduced to zero, and very effective insulation is attained.

The method of correcting the measurements of temperature for radiation is due to Regnault, and depends on the following considerations. The change of temperature produced in the calorimeter by radiation may be regarded as a linear function of the temperature for the small range of temperature. If it is known for the two extremes of temperature, simple interpolation will give the effect for any intermediate temperature.

The thermometer is read at regular intervals (about 20 seconds) at the commencement of the experiment. This gives the change at the lowest temperature, if heat is evolved during the reaction. The reaction is then started at one of these intervals, and the thermometer is read in the same manner, until the temperature change is again proportional to the time. The reaction is then at an end, and the change at very nearly the highest temperature is also known. By adding on the proportional losses for the intermediate temperatures during the reaction, we can calculate the final temperature which would have been attained if no loss of heat by radiation had occurred.

This is the general principle of the method; for details the works on thermochemistry or the larger text-books of physics must be consulted.

Calculation.—The number of heat-units developed in a thermochemical reaction is obtained by multiplying the thermal capacity of the calorimeter by the (corrected) change of temperature. To get the result in the units given above (p. 249), this number has still to be multiplied by the ratio of the substance used to its formula-weight, both being expressed in grams.

With regard to the thermal capacity of the calorimeter, the water-equivalent of the vessel, the stirrer, the thermometer, and all the other parts of the apparatus that suffer the change of temperature must be determined or calculated by multiplying the weights by the specific heats. If the liquid employed is not water, its specific heat must also be known. As the specific heat of a solution is not deducible from the specific heats of the dissolved substance and the solvent, special determinations would in almost all cases have to be made. Thermochemists have hitherto sought to elude the not inconsiderable complication here involved by making certain assumptions, which without a knowledge of the numbers in question lead to fairly accurate calculations. Thomsen puts the thermal capacity of his solutions equal to that of the water contained in them. This assumption, tested in detail by Thomsen himself, is only very seldom quite accurate; but the errors are sometimes positive, sometimes negative, and in all cases very small for dilute solutions, which are nearly always here in question.

An idea of the admissibility of such a procedure may be obtained by calculating the difference between the thermal capacity of aqueous solutions and that of the water contained in them. It will be found that the difference usually does not amount to one per cent—only in extreme cases is it greater. The accuracy of calorimetric experiments varies a good deal, but it is often greater than this, so that it cannot be denied that the results are somewhat impaired by the above mode of calculation.

In the units employed in the calculations which follow, the thermal capacity of 1 g. of water is ·004183 kj.

To find the observed thermal effect we have the formula

$$Q = (t_c - t_a)a + (t_c - t_b)(b + p),$$

where t_a is the temperature of the substance outside the calorimeter proper, t_b of that within the calorimeter, and t_c the corrected final temperature after the reaction; a is the calorimetric equivalent of the first substance, b that of the second (*i.e.* in the mixture-calorimeter the quantities of water in the solutions employed). Lastly, p is the water-equivalent of the calorimeter.

Thus, for example, the heat of neutralisation of hydrochloric acid with soda was found by Thomsen to be 57·5 kj., by mixing $\frac{1}{8}$ formula-weight or $\frac{1}{4}$ equivalent of each of two solutions having the composition $Na_2O + 200H_2O$ and $H_2Cl_2 + 200\ H_2O$, with one another. The solution in the calorimeter had a temperature of 18°·610; the solution in the upper vessel was at 18°·222; after mixing the corrected temperature was 22°·169. The solutions had consequently experienced a rise of temperature of 3°·559 and 3°·947 respectively. Multiplying these by the factor ·004183 and the weight of water, 450 g. $(=\frac{1}{8} \times 200H_2O)$, 13 g. being added to the first solution as the water-equivalent of the calorimeter, we obtain $6{\cdot}90 + 7{\cdot}47 = 14{\cdot}37$ kj., so that multiplying this value by 4, as only $\frac{1}{4}$ equivalent was used, we get 57·48 kj. as the heat of neutralisation of one equivalent of soda by one equivalent of hydrochloric acid, or

$$NaOH\ Aq + HCl\ Aq = NaCl\ Aq + 57{\cdot}5\ kj.$$

Berthelot diverges from Thomsen's method, inasmuch as he does not determine the thermal capacity of his solutions according to the weight of water, but according to the total volume. He consequently does not use solutions of the composition indicated by certain ratios of the formula-weights, but such as are employed in volumetric analysis, a mol of the substance being contained in a litre, or in a multiple or sub-multiple of a litre. The approximation to the truth obtained by this mode of reckoning is in some cases greater than that got from the method practised by Thomsen; in other cases, however, it is just the reverse. On the whole, Berthelot's method is more convenient in practice.

The Influence of Temperature.—The effect of temperature on the numerical values obtained is an important question in thermochemistry. As a rule, the differences of energy vary in amount with the temperature, the reason being that the thermal capacity of the initial substances is not the same as that of the final products. If the former is the greater, more heat is required to warm them up than to warm up the products, and the evolution of heat will increase with rise of temperature. If the products have a greater thermal capacity than the initial substances, the converse holds.

According to the law of Neumann and Kopp (p. 208) the thermal capacity of compounds is independent of their nature and is equal to the sum of the thermal capacities of the components, so that the initial and final substances should have the same capacity. If this were so, the evolution of heat would be independent of the temperature. But the law holds for solids only; and even then only approximately; if a change of state occurs, or if a liquid takes part in the reaction, the law loses its validity, and the thermal effect varies with the temperature.

To express this in a formula, let Q_1 be the thermal effect at the temperature t_1, and Q_2 at t_2; and the thermal capacities of the initial substance and of the final products, K and K_1 respectively. According to the First Law the difference of energy must be the same in whatever way the reaction is carried out. We allow it to take place at t_1, and obtain the thermal effect Q_1. We then warm the initial substances from t_1 to t_2, the amount of heat taken up being $K(t_2 - t_1)$. The reaction then takes place at t_2 and yields Q_2. The products are cooled to t_1, the evolution of heat amounting to $K_1(t_2 - t_1)$. The sum must be equal to Q_1, since the initial and final states are the same. We have, therefore, as the desired formula

$$Q_2 = Q_1 + (K - K_1)(t_2 - t_1).$$

It was first established by Kirchhoff.

Thermochemistry of the Non-metals.—As a knowledge of the changes of energy occurring during chemical processes is of importance in many scientific and technical questions, a large number of data has been accumulated to an extent unequalled in any other branch of general chemistry. Notwithstanding this, the discovery of general laws has not kept up with the quantity of material. With the exception of the half-quantitative relation, already mentioned, that the amount of heat evolved during reactions in which analogous substances take part, is a periodic function of the atomic weight of the elements concerned, there is hardly a single thermochemical law of any extent.

This is because the differences of energy which occur during chemical reactions have not the character of natural constants, but depend to very different extents on the temperature. The thermal effects determined at an average temperature of 18° are, therefore, in a manner accidental values, and a different view would be obtained by selecting some other temperature. For this reason, the numerical relations, which have been supposed by various investigators to exist, not only have no claim to strict accuracy, but must be regarded in most cases as accidental, at least unless the effect of temperature in that particular case has been fully established.

Only in organic chemistry, where the great similarity of homologous substances is reflected in their energy relations, and in the phenomena of salt formation have more comprehensive regularities been discovered; these will be referred to in the proper place. For the rest, little more can be given in the following pages than a collection of heats of formation, the substances being in the state of aggregation which they assume at 18° and atmospheric pressure. From these we can deduce by easy calculations the thermal changes accompanying the most diverse reactions (p. 252), so that the tables given represent very nearly all the known data of thermochemistry.[1]

§ 1. **Oxygen.**		Heat of Formation.
1. Ozone	O_3	– 140 kj. (approx).

The formation of ozone from ordinary oxygen is accompanied by considerable absorption of heat.

§ 2. **Hydrogen.**

1. Water	H_2O	286 kj. (liquid).

Latent heat of fusion – 6·0 kj., heat of vaporisation at 100° – 40·5 kj.

2. Hydrogen peroxide	H_2O_2	190 kj.

The heat of formation of the peroxide is less than that of water; consequently the former passes into the latter and free oxygen, with an evolution of 96 kj.

§ 3. **Chlorine.**

1. Chlorine. The heat of vaporisation at – 22° is – 10 kj. for a combining weight.

2. Hydrogen chloride	HCl	92 kj. gas?

Heat of vaporisation at the boiling-point – 15 kj.

Water absorbs the gas with evolution of 72 kj.; the heat of formation in solution is 164 kj.

3. Hypochlorous acid	Cl_2O	– 75 kj.
of	HClO,Aq	125 ,,

The heat solution of the anhydride is 39 kj.

4. Chloric acid	$HClO_3$,Aq	100 kj.
5. Perchloric acid	$HClO_4$,Aq	164 ,,

The anhydrous acid dissolves in water with evolution of 85 kj.; its heat of formation is therefore 79 kj.

§ 4. **Bromine.**

1. Bromine. The heat of fusion is – 5·4 kj., and the heat of vaporisation at the boiling-point 63°, – 14·7 kj.

2. Hydrogen bromide	HBr	50 kj.

The bromine is here taken as gas. For liquid bromine the heat of formation is 35·2 kj. Water absorbs hydrogen bromide with evolution of 84 kj. Heat of vaporisation is – 17 kj.

3. Hypobromous acid	HBrO,Aq	123 kj.

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[1] For all details the reader is referred to the author's *Lehrbuch der allgemeinen Chemie*, vol. ii., Leipzig, Engelmann.

		Heat of Formation.
4. Bromic acid	$HBrO_3,Aq$	67 kj.

In both cases the bromine is taken in the gaseous state.

5. Bromine chloride	BrCl	3 kj.

§ 5. Iodine.

1. Iodine. Heat of fusion, − 6·3 kj.; heat of vaporisation, − 12·8 kj. Boltzmann has calculated the heat of dissociation of I_2 into 2 I and found it to be − 119 kj.

2. Hydrogen iodide	HI	− 25·5 kj.

The formation of hydrogen iodide from hydrogen and solid iodine is accompanied by absorption of heat. Gaseous iodine would combine with hydrogen with almost no thermal effect. The gas dissolves in water with evolution of 80 kj., so that the heat of formation of hydriodic acid, HI,Aq, is 55 kj. Heat of vaporisation at the boiling-point − 79 kj.

3. Iodic acid	HIO_3	243 kj.
	HIO_3,Aq	234 ,,

[illegible] acid dissolves in water with absorption of 9·2 kj. For the [illegible] we have the heat of formation—

	I_2O_5	188 kj.
4. [illegible] acid	HIO_4,Aq	199 ,,

T[illegible] of solution of the crystallised acid, $HIO_4.2H_2O$, is only − 6 kj.

5. Iodine monochloride	ICl	24 kj.

It occurs in two forms, the heat of fusion is − 11·2 kj. for the *α* form and − 9·5 kj. for *β*.

6. Iodine trichloride	ICl_3	90 kj.
7. Iodine bromide	IBr	11 ,,

§ 6. Fluorine.

1. Hydrofluoric acid	HF	162 ,,

Heat of vaporisation − 38·6 kj.; heat of solution 51 kj., therefore heat of formation in aqueous solution is 213 kj.

§ 7. Sulphur.

1. Sulphur. Heat of fusion, − 1·39 kj. The various modifications exhibit differences of energy of from 2 to 4 kj.; the monoclinic variety contains 1·71 kj. more than rhombic.

2. Hydrogen sulphide	H_2S	11·3 kj.

The heat of solution in water is 19 kj.; heat of vaporisation at the boiling-point – 19·6 kj.

		Heat of Formation.
3. Sulphurous acid	SO_2	297 kj.

This number is for the rhombic modification of sulphur stable at the ordinary temperature. The dioxide dissolves in water with evolution of 32 kj., so that the heat of formation of the aqueous acid from hydrogen, oxygen, and sulphur is 615 kj. Heat of vaporisation – 25·8 kj.

4. Sulphuric acid	H_2SO_4	807 kj.
	H_2SO_4,Aq	882 ,,
	SO_3	432 ,,
	SO_3,Aq	596 ,,

The heat of solution of sulphuric acid in water is 75 kj., that of the anhydride 164 kj. The heat of fusion of the solid acid is – 9·6 kj.; the heat of vaporisation of the liquid at the boiling-point (326°) is – 54·0 kj.

5. Thiosulphuric acid	$H_2S_2O_3,Aq$	578 kj.
	S_2O_2,Aq	292 ,,
6. Dithionic acid	$H_2S_2O_6,Aq$	1170 ,,
	S_2O_5,Aq	883 ,,
7. Trithionic acid	$H_2S_3O_6,Aq$	1142 ,,
	S_3O_5,Aq	856
8. Tetrathionic acid	$H_2S_4O_6,Aq$	1093
	S_4O_5,Aq	807
9. Pentathionic acid	$H_2S_5O_6,Aq$	1152 ,,
	S_5O_5,Aq	766 ,,
10. Persulphuric acid	$H_2S_2O_8,Aq$	1359 ,,
	S_2O_7,Aq	1073 ,,
11. Sulphur monochloride	S_2Cl_2	60 ,,

Heat of vaporisation – 27·8 kj.

12. Sulphur monobromide	S_2Br_2	4·4 ,,
13. Sulphuryl chloride	SO_2Cl_2	371 ,,
14. Thionyl chloride	$SOCl_2$	197 ,,

Heat of vaporisation – 27·6 kj.

15. Pyrosulphuryl chloride	$S_2O_5Cl_2$	806 ,,

Heat of vaporisation – 31·8 kj.

§ 8. Selenium.

1. Hydrogen selenide	H_2Se	– 106 kj. Heat of solution 39 kj.
2. Selenious acid	SeO_2	239 ,,
	SeO_2,Aq	236 ,,
	H_2SeO_3,Aq	521 ,,

		Heat of Formation.	
3. Selenic acid	SeO_3,Aq	321 kj.	
	H_2SeO_4,Aq	607 ,,	
4. Selenium monochloride	Se_2Cl_2	93 ,,	
5. Selenium tetrachloride	$SeCl_4$	193 ,,	

§ 9. Tellurium.

1. Tellurous acid	TeO_2,Aq	323 ,,	Heat of solution 0
	H_2TeO_3,Aq	609 ,,	
2. Telluric acid	TeO_3,Aq	412 ,,	
	H_2TeO_4,Aq	699 ,,	
3. Tellurium tetrachloride	$TeCl_4$	324 ,,	

§ 10. Nitrogen.

1. Ammonia	NH_3	50 ,,
	NH_3,Aq	85 ,,

Heat of vaporisation at 11° is − 21·1 kj.; heat of fusion at − 75° is − 7·7 kj.

2. Nitrous oxide	N_2O	− 75 kj.	
3. Nitrous acid	HNO_2,Aq	129 ,,	
Nitrogen trioxide	N_2O_3	− 90 ,,	
4. Nitric acid	HNO_3,Aq	205 ,,	
	N_2O_5,Aq	2 × 62 ,,	
	HNO_3	174 ,,	Heat of solution 30 kj.

Heat of vaporisation − 21 kj.

	N_2O_5	50 ,,	Heat of solution 70 kj.

The heat of fusion of nitrogen pentoxide is − 35 kj., the heat of vaporisation − 20 kj. The sum of these two equals the heat of formation of the solid pentoxide, so that the heat of formation of the gaseous pentoxide is almost nil, − 5 kj.

5. Nitrogen peroxide			
	N_2O_4	− 11 kj.	Heat of fusion − 13 kj.
	NO_2	− 32 ,,	

The heat of dissociation of N_2O_4 into $2NO_2$ is − 54 ,,

6. Nitric oxide	NO	− 90 ,,
7. Hydroxylamine	NH_3O,Aq	102 ,,
8. Hydrazin	N_2H_6O	269 ,,
	N_2H_4,Aq	9 ,,
	N_2H_6O,Aq	277 ,,

§ 11. Phosphorus.

1. Phosphorus. The transformation of yellow phosphorus into red is accompanied by evolution of 114 kj.

		Heat of Formation.	
2. Phosphoric acid	H_3PO_4	1267 kj.	
	H_3PO_4,Aq	1278 „	
	P_2O_5,Aq	2 × 849 „	
Pyrophosphoric acid	$H_4P_2O_7$	2245 kj.	Heat of solution 30 kj.
Metaphosphoric acid	HPO_3	959 „	Heat of solution 43 kj.
3. Phosphorous acid	H_3PO_3	952 „	
	H_3PO_3,Aq	951 „	
	P_2O_3,Aq	2 × 523 „	
4. Hypophosphorous acid	H_3PO_2	586 „	
	H_3PO_2,Aq	585 „	
	P_2O,Aq	2 × 156 „	
5. Hydrogen phosphide	PH_3	18 „	Heat of vaporisation – 17·2 kj.
6. Phosphonium bromide	PH_4Br	145 „	
7. Phosphonium iodide	PH_4I	93 „	
8. Phosphorus trichloride	PCl_3	316 „	Heat of vaporisation – 28·9 kj.
9. Phosphorus pentachloride	PCl_5	448 „	
10. Phosphorus oxychloride	$POCl_3$	608 „	
11. Phosphorus tribromide	PBr_3	187 „	
12. Phosphorus pentabromide	PBr_5	247 „	
13. Phosphorus oxybromide	$POBr_3$	442 „	
14. Phosphorus iodide	PI_2	41 „	
15. Phosphorus tri-iodide	PI_3	46 „	

§ 12. Arsenic.

1. Arsenic acid	As_2O_5	918 „	Heat of solution 25 kj.
	As_2O_5,Aq	2 × 471 „	
	H_3AsO_4,Aq	901 „	
2. Arsenious acid	As_2O_3	647 „	Heat of solution – 32 kj.
	AsO_2,Aq	450 „	
3. Hydrogen arsenide	AsH_3	– 185 „	
4. Arsenic trichloride	$AsCl_3$	299 „	Heat of vaporisation – 35 kj.

		Heat of Formation.	
5. Arsenic tribromide	$AsBr_3$	188 kj.	
6. Arsenic tri-iodide	AsI_3	53 ,,	

§ 13. Antimony.

1. Antimony trichloride	$SbCl_3$	382 ,,	Heat of fusion − 12·6 kj.
2. Antimony pentachloride	$SbCl_5$	439 ,,	
3. Antimony oxychloride	$Sb_2O_2Cl_2$	753 ,,	
4. Antimony trioxide	Sb_2O_3	697 ,,	
5. Antimony pentoxide	Sb_2O_5	957 ,,	(hydrated oxide)
6. Antimony tribromide	$SbBr_3$	276 ,,	
7. Antimony tri-iodide	SbI_3	104 ,,	
8. Antimony trisulphide	Sb_2S_3	145 ,,	

§ 14. Boron.

1. Boron trichloride	BCl_3	435 ,,
2. Boron trioxide	B_2O_3	1326 ,,
	B_2O_3,Aq	1401 ,,
Boron trisulphide	B_2S_3	346 ,,

The numbers are for amorphous boron and are not very trustworthy.

§ 15. Carbon.

The different modifications of carbon—diamond, graphite, and amorphous carbon—contain different amounts of energy. The greatest is possessed by charcoal,—graphite has about 10 kj. less. Charcoal therefore evolves 10 kj. more on combustion than graphite.

Berthelot and Petit found the heat of combustion of diamond to be 394 kj.; it contains 12 kj. less energy than amorphous carbon.

1. Carbon dioxide	CO_2	406 kj. (from amorphous carbon)

Heat of solution 25 kj.

2. Carbon monoxide	CO	122 ,,

It is somewhat surprising that the first oxygen atom that combines with the carbon evolves much less heat than the second, the numbers being 122 and 284. It has been suggested that the two heats of combination are really equal, and that the difference of 162 kj. only serves to transform solid carbon into the gaseous state.

3. Methane	CH_4	91 kj.
4. Carbonyl chloride	$COCl_2$	231 ,,
5. Carbon tetrachloride	CCl_4	87 ,,
6. Carbonyl sulphide	COS	155 ,,
7. Carbon disulphide	CS_2	− 82 ,,

The heat of formation of carbon disulphide is negative, *i.e.* carbon burns in sulphur with absorption of heat. The figures refer to amorphous carbon.

		Heat of Formation.
8. Cyanogen	C_2N_2	– 275 kj.
9. Hydrocyanic acid	HCN	– 115 „
10. Cyanic acid	$HCNO,Aq$	155 „
11. Cyanamide	$NH_2.CN$	– 35 „

§ 16. **Silicon.**

Crystalline silicon contains 38 kj. more energy than amorphous silicon. The heat of formation of all the silicon compounds is still very uncertain, so that the values found need not be given here.

Thermochemistry of the Metals.—As in the previous section, the heats of formation of the most important compounds are brought together in the following tables. The few general regularities deduced from these numbers will be dealt with in the succeeding section on salt formation; for the rest, the tables need no explanation. The heat of formation does not include the heat of hydration in the cases in which the salt has water of crystallisation.

§ 1. **Potassium.**

			Heat of Formation.	Heat of Solution.
1.	Potassium hydroxide	KOH	432 kj.	
		KOH,Aq	487 „	
		K_2O,Aq	2 × 344 „	
2.	„ chloride	KCl	436 „	– 18kj.
3.	„ chlorate	$KClO_3$	401 „	– 31 „
4.	„ perchlorate	$KClO_4$	470 „	– 42 „
5.	„ bromide	KBr	398 „	– 21 „
6.	„ bromate	$KBrO_3$	352 „	– 41 „
7.	„ iodide	KI	335 „	– 21 „
8.	„ iodate	KIO_3	521 „	– 28 „
9.	„ fluoride	KF	463 „	– 15 „
10.	„ cyanide	KCN	136 „	– 12 „
11.	„ thiocyanate	$KSCN$	367 „	– 25 „
12.	„ sulphide	K_2S	423 „	42 „
13.	„ hydrogen sulphide	KHS	261 „	3 „
14.	„ sulphite	K_2SO_3	1151 „	6 „
15.	„ pyrosulphite	$K_2S_2O_5$	1555 „	– 47 „
16.	„ sulphate	K_2SO_4	1442 „	– 27 „
17.	„ hydrogen sulphate	$KHSO_4$	1161 „	– 16 „
18.	„ pyrosulphate	$K_2S_2O_7$	1303 „	– 16 „
19.	„ persulphate	$K_2S_2O_8$	1900 „	– 61 „
20.	„ thiosulphate	$K_2S_2O_3$	1161 „	– 21 „
21.	„ nitrate	KNO_3	500 „	– 36 „
22.	„ carbonate	K_2CO_3	1165 „	27 „
23.	„ hydrogen carbonate	$KHCO_3$	974 „	– 22 „

§ 2. **Sodium.**

			Heat of Formation.	Heat of Solution.
1.	Sodium hydroxide	$NaOH$	426 kj.	
		$NaOH,Aq$	468 ,,	
	,, monoxide	Na_2O	419 ,,	230 kj.
2.	,, peroxide	Na_2O_2	503 ,,	
3.	,, chloride	$NaCl$	408 ,,	– 5 ,,
4.	,, hypochlorite	$NaOCl,Aq$	349 ,,	
5.	,, chlorate	$NaClO_3$	363 ,,	– 23 ,,
6.	,, perchlorate	$NaClO_4$	420 ,,	– 15 ,,
7.	,, bromide	$NaBr$	359 ,,	– 1 ,,
8.	,, iodide	NaI	289 ,,	5 ,,
9.	,, fluoride	NaF	430 ,,	– 2 ,,
10.	,, cyanide	$NaCN$	95 ,,	– 2 ,,
11.	,, sulphide	Na_2S	364 ,,	63 ,,
12.	,, hydrogen sulphide	$NaHS$	226 ,,	18 ,,
13.	,, thiosulphate	$Na_2S_2O_3.5aq$	1109 ,,	– 48 ,,
14.	,, sulphite	Na_2SO_3	1123 ,,	– 10 ,,
15.	,, sulphate	Na_2SO_4	1375 ,,	1 ,,
16.	,, hydrogen sulphate	$NaHSO_4$	1120 ,,	– 5 ,,
17.	,, nitrate	$NaNO_3$	466 ,,	– 21 ,,
18.	,, phosphate	Na_2HPO_4	1731 ,,	23 ,,
19	,, carbonate	Na_2CO_3	1140 ,,	23 ,,
20.	,, hydrogen carbonate	$NaHCO_3$	962 ,,	– 18 ,,
21.	,, borate	$Na_2B_4O_7$	3125 ,,	– 44 ,,

§ 3. **Ammonium.**

1.	Ammonium chloride	NH_4Cl	317 ,,	– 17 ,,
2.	,, bromide	NH_4Br	274 ,,	– 18 ,,
3.	,, iodide	NH_4I	206 ,,	– 15 ,,
4.	,, hydrosulphide	NH_4HS	164 ,,	
5.	,, sulphate	$(NH_4)_2SO_4$	1181 ,,	– 11 ,,
6.	,, nitrate	NH_4NO_3	368 ,,	– 26 ,,
7.	,, nitrite	NH_4NO_2	272 ,,	– 20 ,,

§ 4. **Lithium.**

1.	Lithium hydroxide	$LiOH$	466 ,,	24 ,,
2.	,, chloride	$LiCl$	392 ,,	35 ,,
3.	,, sulphate	Li_2SO_4	1398 ,,	25 ,,
4.	,, nitrate	$LiNO_3$	467 ,,	1 ,,

§ 5. **Barium.**

1.	Barium hydroxide	$Ba(OH)_2$	913 ,,	51 ,,
2.	,, monoxide	BaO	533 ,,	144 ,,
3.	,, dioxide	BaO_2	606 ,,	
4.	,, chloride	$BaCl_2$	829 ,,	9 ,,
5.	,, chlorate	$Ba(ClO_3)_2$	734 ,,	– 28 ,,

			Heat of Formation.	Heat of Solution.
6.	Barium bromide	$BaBr_2$	725 kj.	21 kj.
7.	„ sulphide	BaS	424 „	
8.	„ sulphate	$BaSO_4$	428 „	
9.	„ nitrite	$Ba(NO_2)_2$	762 „	– 24 „
10.	„ nitrate	$Ba(NO_3)_2$	960 „	– 39 „
11.	„ carbonate	$BaCO_3$	1200 „	

§ 6. Strontium.

1.	Strontium hydroxide	$Sr(OH)_2$	897 „	49 „
2.	„ oxide	SrO	537 „	123 „
3.	„ chloride	$SrCl_2$	772 „	46 „
4.	„ bromide	$SrBr_2$	659 „	67 „
5.	„ iodide	SrI_2	470 „	86 „
6.	„ sulphide	SrS	408 „	
7.	„ sulphate	$SrSO_4$	1384 „	
8.	„ nitrate	$Sr(NO_3)_2$	919 „	– 19 „
9.	„ carbonate	$SrCO_3$	1176 „	

§ 7. Calcium.

1.	Calcium hydroxide	$Ca(OH)_2$	958 „	13 „
				Heat of Hydration.
2.	„ oxide	CaO	611 „	65 kj.
				Heat of Solution.
3.	„ chloride	$CaCl_2$	760 „	73 kj.
4.	„ bromide	$CaBr_2$	648 „	10 „
5.	„ iodide	CaI_2	510 „	116 „
6.	„ fluoride	CaF_2	455 „	
7.	„ sulphide	CaS	435 „	
8.	„ sulphate	$CaSO_4$	1389 „	20 „
9.	„ nitrate	$Ca(NO_3)_2$	908 „	17 „
10.	„ carbonate	$CaCO_3$	1192 „	
11.	„ carbide	CaC_2	– 30 „	

§ 8. Magnesium.

1.	Magnesium hydroxide	$Mg(OH)_2$	909 „	
2.	„ oxide	MgO	602 „	
3.	„ chloride	$MgCl_2$	632 „	150 „
4.	„ bromide	$MgBr_2$	510 „	181 „
5.	„ iodide	MgI_2	355 „	208 „
6.	„ sulphide	MgS	324 „	
7.	„ sulphate	$MgSO_4$	1265 „	85 „
8.	„ nitrate	$Mg(NO_3)_2.6aq$	881 „	– 18 „
9.	„ ammonium phosphate	$MgNH_4PO_4$	3760 „	
10.	„ carbonate	$MgCO_3$	1115 „	

§ 9. **Aluminium.**

			Heat of Formation.	Heat of Solution.
1.	Aluminium hydroxide	$Al(OH)_3$	1242 kj.	
2.	,, oxide	Al_2O_3	1590 ,,	
3.	,, chloride	$AlCl_3$	674 ,,	321 kj.
4.	,, bromide	$AlBr_3$	502 ,,	375 ,,
5.	,, iodide	AlI_3	295 ,,	327 ,,
6.	,, fluoride	AlF_3	1040 ,,	
7.	,, sulphide	Al_2S_3	512 ,,	

§ 10. **Manganese.**

1.	Manganous hydroxide	$Mn(OH)_2$	683 ,,	
2.	,, oxide	MnO	380 ,,	
3.	Manganese dioxide	MnO_2	526 ,,	
4.	Manganous chloride	$MnCl_2$	469 ,,	67 ,,
5.	,, sulphide	$MnS.aq$	186 ,,	(hydrated sulphide)
6.	,, sulphate	$MnSO_4$	1046 ,,	58 kj.
7.	,, carbonate	$MnCO_3$	882 ,,	
8.	Potassium permanganate	$KMnO_4$	816 ,,	– 44 ,,

§ 11. **Iron.**

1.	Ferrous hydroxide	$Fe(OH)_2$	571 ,,	
2.	,, oxide	FeO	270 ,,	
3.	Ferric hydroxide	$Fe(OH)_3$	1910 ,,	
4.	,, oxide	Fe_2O_3	818 ,,	
5.	Ferrosoferric oxide	Fe_3O_4	1107 ,,	
6.	Ferrous chloride	$FeCl_2$	343 ,,	75 ,,
7.	Ferric ,,	$FeCl_3$	402 ,,	133 ,,
8.	Ferrous bromide	$FeBr_2,Aq$	338 ,,	
9.	Ferric ,,	$FeBr_3,Aq$	405 ,,	
10.	Ferrous iodide	FeI_2,Aq	194 ,,	
11.	,, sulphide	$FeS.aq$	100 ,,	(hydrated sulphide)
12.	,, sulphate	$FeSO_4,Aq$	986 ,,	
13.	Ferric sulphate	$Fe_2(SO_4)_3,Aq$	2660 ,,	
14.	Potassium ferrocyanide	$K_4Fe(CN)_6$	575 ,,	– 50 kj.
15.	,, ferricyanide	$K_3Fe(CN)_6$	244 ,,	– 60 ,,

Carbon is taken up by iron (in cast iron) with absorption of heat, silicon with evolution of heat.

§ 12. **Cobalt.**

1.	Cobaltous hydroxide	$Co(OH)_2$	551 kj.	
2.	,, oxide	CoO	153 ,,	
3.	,, chloride	$CoCl_2$	320 ,,	77 kj.
4.	,, sulphide	$CoS.aq$	82 ,,	
5.	,, sulphate	$CoSO_4,Aq$	965 ,,	

§ 13. Nickel.

			Heat of Formation.	Heat of Solution.
1.	Nickel hydroxide	$Ni(OH)_2$	540 kj.	
2.	,, oxide	NiO	250 ,,	
3.	,, chloride	$NiCl_2$	312 ,,	80 kj.
4.	,, sulphide	$NiS.aq$	73 ,,	
5.	,, sulphate	$NiSO_4,Aq$	960 ,,	

§ 14. Zinc.

1.	Zinc oxide	ZnO	359 ,,	
2.	,, hydroxide	$Zn(OH)_2$	632 ,,	
3.	,, chloride	$ZnCl_2$	407 ,,	65 ,,
4.	,, bromide	$ZnBr_2$	318 ,,	63 ,,
5.	,, iodide	ZnI_2	206 ,,	47 ,,
6.	,, sulphide	$ZnS.aq$	166 ,,	
7.	,, sulphate	$ZnSO_4$	962 ,,	77 ,,
8.	,, nitrate	$Zn(NO_3)_2,Aq$	554 ,,	

§ 15. Cadmium.

1.	Cadmium hydroxide	$Cd(OH)_2$	561 ,,	
2.	,, chloride	$CdCl_2$	390 ,,	13 ,,
3.	,, bromide	$CdBr_2$	315 ,,	2 ,,
4.	,, iodide	CdI_2	204 ,,	– 4 ,,

The halogen compounds of cadmium do not obey the law of thermoneutrality; the heats of neutralisation for two equivalents of hydrochloric, hydrobromic, and hydriodic acid are respectively 85, 90, and 101 kj., instead of being equal, as is the case with most of the corresponding salts. The cause is the small degree of ionisation of these salts, the iodide being the least ionised.

5.	Cadmium sulphide	$CdS.aq$	126 kj.	
6.	,, sulphate	$CdSO_4$	935 ,,	45 kj.
7.	,, nitrate	$Cd(NO_3)_2,Aq$	486 ,,	
8.	,, carbonate	$CdCO_3$	761 ,,	

§ 16. Copper.

1.	Cupric oxide	CuO	156 ,,	
2	Cuprous ,,	Cu_2O	171 ,,	
3.	Cupric chloride	$CuCl_2$	216 ,,	46 ,,
4.	Cuprous ,,	Cu_2Cl_2	275 ,,	
5.	Cupric bromide	$CuBr_2$	137 ,,	35 ,,
6.	Cuprous ,,	Cu_2Br_2	209 ,,	
7.	,, iodide	Cu_2I_2	136 ,,	
8.	,, sulphide	Cu_2S	76 ,,	
9.	Cupric sulphide	CuS	42 ,,	
10.	,, sulphate	$CuSO_4$	764 ,,	66 ,,
11.	,, nitrate	$Cu(NO_3)_2,Aq$	344 ,,	

§ 17. Mercury.

By choosing an unsuitable method, Thomsen obtained for the heat of formation of the mercury compounds values which were affected by a considerable error. Nernst (1888) has made more accurate determinations.

			Heat of Formation.	Heat of Solution.
1.	Mercurous oxide	Hg_2O	93 kj.	
2.	Mercuric ,,	HgO	87 ,,	
3.	Mercurous chloride	Hg_2Cl_2	262 ,,	
4.	Mercuric ,,	$HgCl_2$	223 ,,	– 14 kj.
5.	Mercurous bromide	Hg_2Br_2	205 ,,	– 14 ,,
6.	Mercuric ,,	$HgBr_2$	169 ,,	
7.	Mercurous iodide	Hg_2I_2	119 ,,	
8.	Mercuric ,,	HgI_2	102 ,,	
9.	,, cyanide	$Hg(CN)_2$	– 240 ,,	– 12·5 ,,
10.	Mercurous sulphate	Hg_2SO_4	725 ,,	
11.	Mercuric ,,	$HgSO_4$	692 ,,	

The halogen compounds of mercury, like those of cadmium, and for the same reason, do not obey the law of thermoneutrality.

12. Mercuric sulphide HgS 26 kj.

13. Amalgams. The alkali metals combine with mercury with great evolution of heat. Solid potassium amalgam KHg_{12} has a heat of formation of 142 kj.; sodium amalgam, $NaHg_6$, 88 kj. As potassium on combining with mercury evolves much more heat than sodium, sodium amalgam acting on water or acids gives out about 25 kj. more than potassium amalgam.

§ 18. Silver.

1.	Silver oxide	Ag_2O	25 kj.	
2.	,, chloride	$AgCl$	123 ,,	– 67 kj.
3.	,, bromide	$AgBr$	95 ,,	– 85 ,,
4.	,, iodide	AgI	58 ,,	
5.	,, cyanide	$AgCN$	– 132 ,,	
6.	Potassium silver cyanide	$KAg(CN)_2$	54 ,,	– 35 ,,
7.	Silver sulphide	Ag_2S	14 ,,	
8.	,, sulphate	Ag_2SO_4	700 ,,	– 19 ,,
9.	,, carbonate	Ag_2CO_3	514 ,,	
10.	,, nitrate	$AgNO_3$	120 ,,	– 23 ,,

§ 19. Thallium.

1.	Thallous oxide	Tl_2O	177 ,,	– 13 ,,
2.	,, hydroxide	$TlOH$	238 ,,	– 13 ,,
3.	,, chloride	$TlCl$	203 ,,	– 42 ,,
4.	,, bromide	$TlBr$	173 ,,	
5.	,, iodide	TlI	126 ,,	
6.	,, sulphide	Tl_2S	82 ,,	

			Heat of Formation.	Heat of Solution.
7.	Thallous sulphate	Tl_2SO_4	924 kj.	– 35 kj.
8.	,, nitrate	$TlNO_3$	243 ,,	– 42 ,,
9.	Thallic hydroxide	$Tl(OH)_3$	610 ,,	
10.	,, chloride	$TlCl_3,Aq$	373 ,,	
11.	,, bromide	$TlBr_3,Aq$	236 ,,	
12.	,, iodide	TlI_3,Aq	45 ,,	

§ 20. Lead.

1.	Lead oxide	PbO	210 ,,	
2.	,, peroxide	PbO_2	260 ,,	
3.	,, chloride	$PbCl_2$	346 ,,	– 28 ,,
4.	,, bromide	$PbBr_2$	270 ,,	– 42 ,,
5.	,, iodide	PbI_2	167 ,,	
6.	,, sulphide	PbS	85 ,,	
7.	,, sulphate	$PbSO_4$	904 ,,	
8.	,, nitrate	$Pb(NO_3)_2$	441 ,,	– 34 ,,
9.	,, carbonate	$PbCO_3$	711 ,,	

§ 21. Bismuth.

1.	Bismuth trichloride	$BiCl_3$	380 ,,	
2.	,, oxychloride	$BiOCl$	369 ,,	
3.	,, hydroxide	$Bi(OH)_3$	718 ,,	

§ 22. Tin.

1.	Stannous hydroxide	$Sn(OH)_2$	571 ,,	
2.	,, chloride	$SnCl_2$	338 ,,	1 ,,
3.	Stannic chloride	$SnCl_4$	532 ,,	120 ,,

§ 23. Gold.

The gold precipitated from solution comes down in different modifications with variations of energy from 13 kj. to 20 kj. The following numbers refer to the variety with most energy, viz. that precipitated by sulphur dioxide from the chloride.

1.	Auric hydroxide	$Au(OH)_3$	402 kj.	
		$Au_2O_3.aq$	– 55 ,,	
2.	Auric chloride	$AuCl_3$	95 ,,	19 kj.
3.	Chlorauric acid	$HAuCl_4,Aq$	298 ,,	
4.	Auric bromide	$AuBr_3$	37 ,,	– 16 ,,
5.	Bromauric acid	$HAuBr_4,Aq$	172 ,,	
6.	Aurous chloride	$AuCl$	24 ,,	
7.	,, bromide	$AuBr$	0 ,,	
8.	,, iodide	AuI	– 23 ,,	

§ 24. Platinum.

			Heat of Formation.	Heat of Solution.
1.	Platinic chloride	$PtCl_4$	248 kj.	82 kj.
2.	Chloroplatinic acid	H_2PtCl_6,Aq	683 ,,	
3.	Potassium chloroplatinate	K_2PtCl_6	1256 ,,	– 58 ,,
4.	Platinic bromide	$PtBr_4$	177 ,,	
5.	Bromoplatinic acid	H_2PtBr_6,Aq	515 ,,	

The heats of neutralisation of the two acids are the same as that of hydrochloric acid.

6.	Platinic iodide	PtI_4	73 kj.
7.	Chloroplatinous acid	H_2PtCl_4,Aq	503 ,,
8.	Bromoplatinous ,,	H_2PtBr_4,Aq	370 ,,
9.	Platinous hydroxide	$Pt(OH)_2$	361 ,,

§ 25. Palladium.

1.	Palladious hydroxide	$Pd(OH)_2$	381 ,,
2.	Chloropalladious acid	H_2PdCl_4,Aq	529 ,,
3.	Palladious iodide	PdI_2	76 ,,
4.	Palladic hydroxide	$Pd(OH)_4$	699 ,,

Salt Formation and Ionisation.—The regularity observed in all the properties of dilute solutions of salts, that they are the sum of the properties of their constituents or ions, also holds for the most important property of all, the change in the amount of energy, but in a somewhat different form. By analogy, the energy of a salt solution is the sum of two terms, one of which depends only on the kation or metal, the other only on the anion or halogen. This is true; but, as the total amount of energy cannot be measured, only the difference of energy between different states, the rule can only be indirectly tested in its consequences.

The first consequence is that no change in energy occurs when two dilute salt solutions are mixed. For, as the ions remain unchanged in the mixture, no reaction is caused by their presence together, and therefore no heat is evolved.

This law was the first result of the systematic investigation of the thermochemistry of salts undertaken by Hess (1840), and is known as the law of thermoneutrality.

It has since been found not to be strictly true; there are many exceptions, though the law is obeyed in the great majority of cases. The exceptions are related to other properties of solutions, osmotic pressure and allied properties in particular. Stated generally, the law of thermoneutrality holds if the osmotic pressure shows that the ions present are absolutely independent of each other, *i.e.* when the value of i (p. 190) is equal to the number of ions contained in the formula of the salt. The greater the deviation of i from the limiting value, the less closely is the law of thermoneutrality followed.

Observations on the depression of freezing-point of salt solutions have shown that i is nearer the theoretical limit, or, in other words, the salt is more completely ionised, the more dilute the solution is. The law of thermoneutrality is also more exact, the more dilute the solutions are.

In some cases divergences occur in dilute solutions; the halogen compounds of mercury and of cadmium, and many of the cyanides and thiocyanates are instances. All these compounds are found by the other methods to be very feebly ionised.

The peculiar behaviour of acids and bases, which are also to be regarded as salts, is dealt with below: it is caused by the same circumstance.

The law is also departed from if a salt separates out as a solid. The thermal effect is then the sum of the action in solution and of the heat of precipitation of the dissolved salt; the latter is the same as the heat of solution with the sign changed. If the dissolved salts follow the law of thermoneutrality (as can be ascertained from the value of i), the total heat effect is the heat of precipitation; the heats of solution of sparingly soluble salts, which cannot be directly determined, can be measured in this way.

The law of thermoneutrality is never obeyed in the neutralisation of acids and bases: there is always a considerable evolution of heat. For acids and bases, which are practically completely ionised, as shown by their i value, the evolution of heat is very large, amounting to 57 kj.; it is constant, *i.e.* is independent of the nature of the two substances. The following table illustrates this:

		$NaOH$	$LiOH$	KOH	$Ba(OH)_2$	$Sr(OH)_2$	$(CH_3)_4NOH$
Hydrochloric	acid	57 kj.	57 kj.	57 kj.	58 kj.	58 kj.	58 kj.
Hydrobromic	,,	57 ,,	...	...	...	...	...
Hydriodic	,,	57 ,,	...	...	...	...	...
Nitric	,,	57 ,,	...	...	...	...	...
Chloric	,,	58 ,,	...	...	58 ,,	...	...
Bromic	,,	58 ,,	...	...	...	...	...
Chloroplatinic	,,	57 ,,	...	...	58 ,,	...	...
Hyposulphurous	,,	56 ,,	...	...	...	...	...

The explanation of this apparent discrepancy is easily found, if the neutralisation of an acid and a base is explicitly formulated. For hydrochloric acid and sodium hydroxide we have, for instance,

$$HCl + NaOH = NaCl + H_2O.$$

For hydrochloric acid, sodium hydroxide and sodium chloride $i = 2$; three of the four substances are thus completely ionised.[1] Water is not fully ionised; although it can dissociate into $H^{\cdot}$, the ion characteristic of acids, and OH', the ion common to bases, all

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[1] The dissociation is not quite complete, but it is to such an extent that the remainder can be neglected in the present discussion.

the methods hitherto employed indicate that the ions of water are present in exceedingly small quantity, so that water may for our present purpose be regarded as not ionised. While the ions $Na^{\cdot}$ and Cl' remain unchanged during the reaction and thus occasion no heat change, the ions H' and OH' unite to form undissociated water, and the 57 kj. observed is the heat of formation of water from hydrogen and hydroxyl ions.

This heat of formation must not be confused with the heat of formation of water from oxygen and hydrogen. Apart from the fact that it is hydroxyl, and not oxygen, hydrogen in the state of ion is not equivalent to hydrogen gas, as the two have essentially different properties (p. 192), and therefore differ in energy.

Between water, which is extremely little ionised, and most neutral salts, which are fairly completely ionised, come the acids and bases with widely differing degrees of ionisation. In all cases the degree of ionisation increases with dilution; but this does not mask the essential differences.

Although detailed treatment of this matter belongs by right to a later section, the most important classes will be given here, as a knowledge of them greatly facilitates the due comprehension of thermochemistry.

The halogen acids, with the exception of hydrofluoric acid, are very fully ionised, as are also the monobasic oxygen acids of nitrogen and the halogens. Of the dibasic acids chloroplatinic acid and the polythionic acids alone belong to this group; the tribasic acids as a rule belong to the less ionised group. Sulphuric acid is about half ionised at moderate dilutions, the other dibasic acids even less so. Arsenic acid and phosphoric acid are still less ionised. The carboxylic acids of the fatty series are very little dissociated; the presence of halogen, of the nitro- or of the cyanogen group, increases the degree of ionisation, which may be nearly complete (trichloracetic acid).

Among the bases, the hydroxides of the alkalies and of the alkaline earths and thallous hydroxide are almost completely ionised. So are the quaternary ammonium bases, and the analogous compounds of phosphorus, arsenic and antimony and also the sulphine bases. Most other bases, in particular the volatile derivatives of ammonia, are very slightly ionised.

Heat of Neutralisation.—From this point of view, the formation of a salt from an acid and a base, both of which are largely ionised, consists in the formation of water from hydrogen and hydroxyl ions, and the heat evolved is 57 kj. This is what actually occurs when any of the above fully ionised substances are caused to react, provided no precipitate is formed.

If a precipitate is formed, the difference from the value 57 kj. is to be regarded as the heat of solution of the substance (to form a dissociated solution) with the sign changed.

If a feebly ionised acid is neutralised with a fully ionised base without formation of a precipitate, the heat is the sum of two values: the heat of formation of water from its ions, 57 kj., and the heat required to decompose the acid into its ions. The process can be imagined to take place in this way: first the acid is ionised, then the process of neutralisation takes place with this fully ionised acid; as the final result is the same, the two thermal effects must be the same. The difference between the observed heat of neutralisation and the constant 57 kj. is thus the heat of dissociation of the acid.

If the acid is partially ionised, a corresponding fraction of the heat of dissociation is obtained. By estimating this fraction (*e.g.* from the depression of the freezing-point), the heat of dissociation can be calculated.

The same considerations apply to the neutralisation of a partially ionised base with a fully ionised acid; it is unnecessary to repeat them.

If both substances are slightly or not completely ionised, the thermal effect is the sum of the constant 57 kj. and the heats of dissociation of the acid and the base. This is the general case, of which the instances given above are limiting cases.

In this case the heat of neutralisation is expressed by a formula $C + a + b$, in which C is the constant 57 kj., a and b the heats of dissociation of the acid and base. The form is the same whether the acid and base are ionised to a greater or less extent, as it denotes in each case the amount of heat necessary for the complete dissociation of the substance starting from its original condition.

This is exactly what had been found experimentally long before the development of these ideas. Hess assumed, on the discovery of his law of thermoneutrality, that the heat of neutralisation depended only on the acid, the same acid developing the same amount of heat with different bases; the law of thermoneutrality would follow from this. Andrews, who investigated similar questions later, believed, on the other hand, that the base alone determined the heat of neutralisation. Favre and Silbermann showed that both assumptions are wrong, but that the differences between the heats of neutralisation of different acids with a base are independent of the nature of the base. The same holds for the neutralisation of different bases with an acid. This law is identical with the above law, that the heat of neutralisation is expressed by a formula $C + a + b$; for a depends only on the acid, and b only on the base. The heats of neutralisation of different acids with the same base are given by $C + a_1 + b, C + a_2 + b, C + a_3 + b$, etc. The differences between the others and the first are given by $a_1 - a_2$, $a_1 - a_3$, etc., which are independent of b. The same is true of bases.

In addition to the thermal effect of neutralisation, there is another which is observed when a neutral salt is mixed with the corresponding acid or base. It occurs when the latter are only partially ionised, and is due to the effect which the neutral salt exerts on the degree of ionisation. The extent of this influence can be calculated from the theory of chemical equilibrium; it must suffice to state that there is good agreement between the observed and the calculated effect.

The heat of dissociation of a partially ionised acid can be estimated by subtraction of the observed heat of neutralisation with sodium hydroxide (or any other fully ionised base) from the value 57 kj. The heat of dissociation of a base can be obtained in the same way. It is necessary to know in each case the extent of ionisation of the less ionised substance in the given solution.

Although no systematic investigation in this direction has been undertaken, there is sufficient material to permit of a review of the subject. The heat of dissociation is usually inconsiderable, amounting to only a small fraction of the total heat of neutralisation, and seldom exceeding 10 kj. The sign is sometimes positive, at others negative: in some cases the dissociation into ions is accompanied by evolution of heat, in the others by absorption of heat. No simple connexion with other properties has been made out; but according to the general behaviour constitutive influences are to be expected.

Heat of Formation of Ions.—The thermochemistry of salt solutions can be brought into a very simple form, in consequence of the mutual independence of the ions in dilute solution. If the heat of formation of the various ions from the corresponding elements is once determined, the sum of any two of them will give the heat of formation of the corresponding salt in dilute solution.

There is, indeed, no purely thermochemical means of calculating the heat of formation of the single ions. As equivalent amounts of kations and anions must be formed simultaneously, the sum of the two heats of formation is obtained, and the single values cannot be determined. But if the heat of formation of only one ion is known, all the others can be calculated by means of it. For example, if the heat of formation of chloride ion from chlorine gas is known, subtraction of its value from the heat of formation of any chloride in dilute solution will at once give the heat of formation of the metal ion. By means of the value for this metal ion, the heat of formation of any anion which forms a soluble salt with the particular metal can be ascertained in the same way.

Electrochemistry provides such a method of estimating the heat of formation of ions. Details cannot be given, but the result will be used as the basis for the calculation. Should subsequent alteration of this value be found necessary, the same correction would have to be applied to all ions, for only one heat of formation of ion is involved in the calculation from the direct thermochemical data.

It has been observed that a very small amount of heat is required for the conversion of gaseous hydrogen into hydrogen ion; so far as is known at present about 4 kj. are required for H_2. As the number is not certain to this amount, it may provisionally be made zero. Subsequent corrections will then be more easily applied.

It follows at once that the heat of formation of a metal ion is equal to the thermal effect produced by the displacement of hydrogen from a fully ionised acid by the metal, the hydrogen escaping as gas. In this process the metal ion is formed from the metal, and at the same time the hydrogen ion is converted into hydrogen gas. According to the above assumption, the latter process causes no thermal effect, so that the whole of the heat comes from the former transformation.

In consequence of this, the solution of a metal in any fully ionised acid should give the same amount of heat, independently of the nature of the acid. This was early demonstrated by Andrews.

The heats of formation obtained by this method are given in the adjoining table. The heat of formation of a dissolved salt is the sum of the values attached to the two ions of the salt, due regard being paid to the valency of the ions as indicated by the formula. The formulæ of ions are distinguished from those of other substances by means of dots in the case of kations, and dashes in the case of anions, the valency being indicated by the number of dots or dashes. Energy equations can be written for them in the usual manner. The formula

$$[Na] = Na^{\cdot} + 240 \text{ kj.}$$

and

$$(Cl_2) = 2Cl' + 2 \times 164 \text{ kj.}$$

denote that 240 kj. are evolved in the transformation of metallic sodium into sodium ion, and 164 kj. by the transformation of chlorine gas into chloride ion. It must be remembered that ions occur only in dilute solution, so that Aq should be added to the formula. As there are no exceptions to this, the symbol may be omitted without danger of any misunderstanding.

Kations.		Heat of Formation.
Hydrogen	$H^{\cdot}$	0 kj.
Potassium	$K^{\cdot}$	+ 259 ,,
Sodium	$Na^{\cdot}$	+ 240 ,,
Lithium	$Li^{\cdot}$	+ 263 ,,
Rubidium	$Rb^{\cdot}$	+ 262 ,,
Ammonium	$NH_4^{\cdot}$	+ 137 ,,
Hydroxylamine	$NH_4O^{\cdot}$	+ 157 ,,
Magnesium	$Mg^{\cdot\cdot}$	+ 456 ,,
Calcium	$Ca^{\cdot\cdot}$	+ 458 ,,
Strontium	$Sr^{\cdot\cdot}$	+ 501 ,,
Aluminium	$Al^{\cdot\cdot\cdot}$	+ 506 ,,
Manganous	$Mn^{\cdot\cdot}$	+ 210 ,,
Ferrous	$Fe^{\cdot\cdot}$	+ 93 ,,

Kations.		Heat of Formation.
Ferric	$Fe^{\cdot\cdot\cdot}$	− 39 kj.
Cobalt	$Co^{\cdot\cdot}$	+ 71 ,,
Nickel	$Ni^{\cdot\cdot}$	+ 67 ,,
Zinc	$Zn^{\cdot\cdot}$	+ 147 ,,
Cadmium	$Cd^{\cdot\cdot}$	+ 77 ,,
Cuprous	$Cu^{\cdot}$	− 66 ,, (?)
Cupric	$Cu^{\cdot\cdot}$	− 67 ,,
Mercurous	$Hg^{\cdot}$	− 83 ,,
Silver	$Ag^{\cdot}$	− 106 ,,
Thallous	$Tl^{\cdot}$	+ 7 ,,
Lead	$Pb^{\cdot\cdot}$	+ 2 ,,
Stannous	$Sn^{\cdot\cdot}$	+ 14 ,,
Anions.		
Chloride	Cl'	+ 164 ,,
Hypochlorite	ClO'	+ 109 ,,
Chlorate	ClO_3'	+ 98 ,,
Perchlorate	ClO_4'	− 162 ,,
Bromide	Br'	+ 118 ,,
Bromate	BrO_3'	+ 47 ,,
Iodide	I'	+ 55 ,,
Iodate	IO_3'	+ 234 ,,
Periodate	IO_4'	+ 195 ,,
Sulphide	S''	− 53 ,,
Hydrosulphide	HS'	+ 5 ,,
Thiosulphate	S_2O_3''	+ 581 ,,
Dithionate	S_2O_6''	+1166 ,,
Tetrathionate	S_4O_6''	+1093 ,,
Sulphite	SO_3''	+ 633 ,,
Sulphate	SO_4''	+ 897 ,,
Selenide	Se''	− 149 ,,
Selenite	SeO_3''	+ 501 ,,
Selenate	SeO_4''	+ 607 ,,
Telluride	Te''	− 146 ,,
Tellurite	TeO_3''	+ 323 ,,
Tellurate	TeO_4''	+ 412 ,,
Nitrite	NO_2'	+ 113 ,,
Nitrate	NO_3'	+ 205 ,,
Trinitride	N_3'	− 277 ,,
Hypophosphite	H_2PO_2'	+ 603 ,,
Phosphite	HPO_3''	+ 962 ,,
Phosphate	PO_4'''	+1246 ,,
Hydrophosphate	HPO_4''	+1277 ,,
Arsenate	AsO_4'''	+ 900 ,,
Carbonate	CO_3''	+ 674 ,,
Hydrocarbonate	HCO_3'	+ 683 ,,
Hydroxyl	OH'	+ 228 ,,

By means of this small table the heats of formation of about 800 salts in dilute aqueous solution can be calculated.

Organic Compounds.—The thermochemistry of organic compounds is rendered specially interesting by the circumstance that most of the energy used in the industrial arts, as well as all the energy of living organisms, is got from the combustion of organic compounds. The accurate comprehension, therefore, of the economy of these working systems must be preceded by a knowledge of the amount of energy contained in the substances which come under consideration.

Unfortunately the special peculiarity of the processes between carbon compounds, which almost without exception take place slowly, or under pressure at high temperatures, has restricted any extensive research in this domain. There is practically only one method for the determination of the energy in organic compounds, just as there is but one in organic analysis, and that method is the same in both cases, viz. complete combustion. The heat here appearing is the same as that taken into consideration in the first instance in the technical or physiological utilisation of organic substances, and thus the heat of combustion plays a very important part.

If the heat of combustion of an organic compound be subtracted from those of its elements, we obtain, according to the fundamental principle of energy, the heat of combination of the compound from its elements. This has merely an arithmetical significance, as we have scarcely ever been able to form organic compounds directly from their elements. For the purpose of calculating heats of reaction the heats of combustion can, however, be used just as well, for the difference of the heats of combustion of the substances before and after the reaction is equal to the heat developed by the reaction itself, as can also be easily shown from the fundamental principle.

The thermal effects produced by reactions between organic compounds are comparatively small, while the heats of combustion are very great; as the heat of reaction is the difference between the heats of combustion of the substances before and after the reaction, it is got as a small difference of two large numbers, and the experimental error will be correspondingly increased. Heats of combustion must be measured with great accuracy if the results are to be of use.

While the older methods of combustion were liable to unavoidable errors owing to the incompleteness of the combustion even in pure oxygen, Berthelot and Vieille's method of combustion in compressed oxygen has been carried to such a degree of accuracy by Stohmann that heats of reaction can now be deduced with some confidence. No general law of importance has been deduced from the results, and, in particular, there does not appear to be any connexion between the thermal effect and the possibility or the velocity of a reaction.

Laws.—The most general law discovered in this connexion is that heats of combustion are essentially additive in nature. It is not strictly true for this, any more than for any other property, with the sole exception of mass. But the influence of constitution is so slight that its existence was not recognised with certainty before the introduction of the recent accurate methods. The additive nature is most clearly seen in homologous series. Increase of CH_2 causes an increase of 655 kj., and this is so generally true, even in different series, that the difference 655 kj. may be regarded as almost a general constant.

It follows from this relation that the heats of reaction for any one change undergone by different members of a homologous series have always the same value. Writing such a process as the transformation of an alcohol into an acid in the form of an equation, and denoting by A and B the heats of combustion of the substances on the left and right side of the equation, we have $A - B$, equal to the heat of reaction. For a substance with nCH_2 more, which undergoes the same reaction, the corresponding heats of combustion are $A + n655$ kj. and $B + n655$ kj., the difference again amounting to $A - B$.

This circumstance enables us to reduce the thermochemical data of organic chemistry to a very simple form; given the heat of combustion of one member of every occurring type, the numbers for all the homologues (used in a very wide sense) can be calculated by the addition of n655 kj., where n is the (positive or negative) number of carbon atoms in excess of the number contained in the typical substance.

It must be borne in mind that it is only an approximation and that constitution has an effect, although it is small in comparison with the heats of combustion. The numbers calculated in this manner are accurate to about one per cent.

The first member of a homologous series is not so suitable as a typical substance as is a higher member. The explanation of this general phenomenon has been already given (pp. 226 and 232) and can readily be applied to the present case.

Effect of Pressure.—Before proceeding to give experimental results, on which the general relations just mentioned are based, we must take into consideration the effect of external pressure. If a combustion of an organic compound is carried out as usual at constant (atmospheric) pressure, the thermal effect includes not only the difference between the amounts of chemical energy before and after the combustion, but also a certain amount of mechanical work derived from the difference in volume of the substances before and after combustion. If the volume is diminished by combustion, external work is converted into heat, and the observed thermal effect is greater than the difference of chemical energy; in the converse case it is smaller. The two are equal, if there is no change of volume.

We have therefore to distinguish between two different heats of combustion, that at constant volume, which excludes external work, and that at constant pressure, where the external work is included. The older methods of combustion in an open calorimeter gave the latter number, the calorimetric bomb gives the former. The heat of combustion at constant pressure is the only one of importance for physiological and technical purposes, and the appended data refer to constant pressure.

The theoretical objection that the heat of combustion at constant pressure is the sum of two different amounts of energy, chemical and mechanical, while the other represents the chemical energy only, is quite right, but does not detract in the least from the significance of the constant pressure value. Further, the values for constant pressure form a perfectly consistent series of numbers. Systematic errors are not introduced unless the pressure varies during the combustion, and this does not occur in actual practice. It is not at all necessary to have the pressure the same for all the combustions, in order to obtain comparable results; it may vary to any extent, provided that it remains constant throughout each experiment.

The proof of this is as follows; the factor for converting the one number into the other is obtained at the same time. If one mol of a gas is formed, the work expended is independent of the nature of the gas, and is given by the gas equation $pv = RT$ (p. 41). The constant R is $8{\cdot}316 \times 10^7$ in absolute units, and the work is thus 8·316 T joules; it is independent of the pressure and is proportional to the absolute temperature. For the mean temperature of 18° C. or 291° A. it amounts to 2419 j. or 2·42 kj.

If m is the number of mols of gaseous substances before the combustion, and n the number of mols after it, the relation of the heat of combustion at constant pressure, W, to that at constant volume, (W), is

$$(W) = W - (m - n)8{\cdot}316 \text{ Tj.}$$

or at room temperature

$$(W) = W - (m - n)2{\cdot}42 \text{ kj.}$$

Numerical Results.—The data given below afford a brief survey of the most important groups of organic compounds; it does not profess to be a complete record of the work which has been done.

Thomsen found the following heats of combustion for the gaseous hydrocarbons of the methane series:

		Difference.
(CH_4)	886 kj.	
(C_2H_6)	1550 ,,	664 kj.
(C_3H_8)	2214 ,,	664 ,,
(C_4H_{10})	2877 ,,	663 ,,
(C_5H_{12})	3544 ,,	667 ,,

The average increase for each CH_2 is 664 kj. For liquids it is a little larger, since the heat of vaporisation (by which the heat of combustion in the liquid state exceeds that in the gaseous state) slowly rises with increasing molar weight. Stohmann's numbers for liquids are:

		Difference.
C_6H_{14}	4146 kj.	
C_7H_{16}	4830 ,,	684 kj.
$C_{16}H_{34}$	11030 ,,	9 × 689 ,,

The ethylene series is similar. For gases we have:

		Difference.
(C_2H_4)	1395 kj.	
(C_3H_6)	2061 ,,	666 kj.
(C_4H_8)	2722 ,,	661 ,,
(C_5H_{10})	3378 ,,	656 ,,

Liquids of the same series gave:

		Difference.
C_8H_{16}	5239 kj.	
$C_{10}H_{20}$	6677 ,,	2 × 664 kj.

The heat of combustion of acetylene is 1321 kj. If we compare C_2H_2, C_2H_4, C_2H_6, the differences are 74 kj. and 155 kj. The heat of combustion of H_2 is 286 kj.; the union of hydrogen and acetylene takes place with the evolution of 212 kj.; the change from ethylene to ethane also gives out heat (131 kj.).

The heats of combustion of the alcohols are:

		Difference.
CH_4O	714 kj.	
C_2H_6O	1362 ,,	648 kj.
C_3H_8O	2009 ,,	647 ,,
$C_4H_{10}O$	2663 ,,	654 ,,
$C_5H_{12}O$	3321 ,,	658 ,,
$C_8H_{18}O$	5280 ,,	3 × 653 ,,

Propyl glycol, $C_3H_8O_2$, has 1804 kj.; glycerine, $C_3H_8O_3$, has 1662 kj. The change from monohydric to dihydric alcohol diminishes the heat of combustion by 205 kj., from the dihydric to the trihydric alcohol by 142 kj.

The number for isopropyl alcohol is 2000 kj., that of the normal alcohol is 2009 kj.; the small difference is characteristic of the slight effect of isomerism on heats of combustion.

A few important polyhydric alcohols and carbohydrates are:

		kj.			kj.
Erythrite	$C_4H_{10}O_4$	2103	Rhamnose	$C_7H_{12}O_5$	3006
Quercite	$C_5H_{12}O_5$	2972	Mannite	$C_6H_{14}O_6$	3048
Glucose	$C_6H_{12}O_6$	2833	Cane sugar	$C_{12}H_{22}O_{11}$	5668
Milk sugar	$C_{12}H_{22}O_{11}$	5653	Dextrin	$C_6H_{10}O_5$	2791
Starch	$C_6H_{10}O_5$	2865	Cellulose	$C_6H_{10}O_5$	2846

For Aldehydes of the fatty series in the liquid state we have:

		Difference.
C_2H_4O	1127 kj.	
$C_5H_{10}O$	3104 ,,	3 × 659 kj.

For Acetone, C_3H_6O, it is 1772 kj.; diethylketone, $C_5H_{10}O$, 3083 kj.; the difference for CH_2 is 656 kj.

The numbers for the normal fatty acids are:

		Difference.
CH_2O_2	258 kj.	
$C_2H_4O_2$	876 ,,	618 kj.
$C_3H_6O_2$	1537 ,,	661 ,,
$C_4H_8O_2$	2194 ,,	657 ,,
$C_5H_{10}O_2$	2852 ,,	658 ,,
$C_6H_{12}O_2$	3503 ,,	651 ,,

The anomalous value of the first member is very striking.

The heats of combustion of the oxalic acid series are:

		Difference.
$C_2H_2O_4$	251 kj.	
$C_3H_4O_4$	867 ,,	616 kj.
$C_4H_6O_4$	1492 ,,	625 ,,
$C_5H_8O_4$	2154 ,,	662 ,,
$C_6H_{10}O_4$	2798 ,,	644 ,,
$C_7H_{12}O_4$	3467 ,,	669 ,,
$C_8H_{14}O_4$	4114 ,,	647 ,,
$C_9H_{16}O_4$	4774 ,,	660 ,,
$C_{10}H_{18}O_4$	5410 ,,	636 ,,

The first two members of the series are again irregular. The alternation of the differences between the higher homologues corresponds to many similar differences in properties (*e.g.* the melting-points) of acids with odd and even numbers of carbon atoms.

The substances derived from the combination of the alcohols with themselves, and with acids, with loss of water—the simple and compound ethers—have mostly a heat of combustion differing but little from the sum of the heats of combustion of their components, showing that these actions take place with very slight thermal change. The thermal change which does take place has often the negative sign, *i.e.* the substances absorb heat on combination.

Thus the heat of combustion of ethyl ether $(C_2H_5)_2O$ is 2726 kj., while twice that of alcohol is 2724 kj., and the thermal effect of the direct formation of ether is practically zero.

The numbers obtained from the comparison of the heats of combustion of the esters and of the alcohols and acids are similar. The former are mostly from 4 to 8 kj. greater than the sum of the latter, these differences represent the heat of reaction. Thus the heat of combustion of ethyl acetate is 2246 kj., that of acetic acid and alcohol together 2238 kj.; for ethyl butyrate it is 3561 kj., the sum of the acid and alcohol is 3556 kj. This rule may be used to calculate approximately the heats of combustion of organic compounds formed with loss of the elements of water.

Very little of a general character can be said of the organic nitrogen compounds. It is remarkable that a considerable absorption of heat accompanies the formation of cyanogen from its elements. The heat of combustion of $(CN)_2$ is 1086 kj., while that of two atoms of carbon is 788 kj.; the considerable quantity of 298 kj. is thus taken up. In this respect cyanogen resembles acetylene, which likewise is formed at high temperatures with great absorption of heat (of 247 kj., as the heat of combustion is 1321 kj.).

When cyanogen combines with hydrogen, 45 kj. are evolved per atom of hydrogen. This number is near the number for hydrogen bromide. The heat of formation from the elements remains negative.

The heats of combustion of the nitrogenous final products of metabolism in the animal are given by Stohmann as follows:

Urea	$CO(NH_2)_2$	636 kj.
Uric acid	$C_5H_4N_4O_3$	1924 ,,
Hippuric acid	$C_9H_9NO_3$	4242 ,,

The combustion of 1 g. of albumin develops 2·3 to 2·5 kj.

The heat of combustion of numerous aromatic compounds has also been determined. The chief results have exactly the same form as in the case of the fatty compounds, so that only a cursory notice is necessary.

The heat of combustion of benzene is 3260 kj. With the homologues of benzene we again see the increase of about 655 kj. for each CH_2, the different isomers showing no great variation. A few heats of combustion, determined by Stohmann, for other aromatic substances, may serve to give a general idea of the relations here involved.

Phenol	C_6H_6O	3082 kj.
Pyrocatechin Resorcin Hydroquinone	$C_6H_6O_2$	2865 ,, 2857 ,, 2857 ,,
Pyrogallol	$C_6H_6O_3$	2635 ,,
Benzoic acid	$C_7H_6O_2$	3228 ,,
,, aldehyde	C_7H_6O	3521 ,,
,, alcohol	C_7H_8O	3744 ,,
Phthalic acid	$C_8H_6O_4$	3234 ,,
Salicylic acid	$C_7H_6O_3$	3052 ,,

The rules given above are here also generally obeyed. It is remarkable that while the three isomeric cresols, $CH_3.C_6H_4.OH$, have the same heat of combustion, the metameric anisol, $C_6H_5.OCH_3$, differs considerably from them. It is evident from the comparison of pyrocatechin with the other dihydroxybenzenes that not all position-isomers have the same heat of combustion.

We may calculate the heats of combustion of the homologues of the above compounds with sufficient accuracy by adding 655 kj. for every increase of CH_2.

A remarkable general relation has been discovered by Stohmann to exist between the heat of combustion of acids and their chemical "strengths" or affinity constants (see below): the two increase or decrease simultaneously in the case of isomeric acids. As the general relations between chemical composition and the affinity constant are known, it is possible to estimate approximately the difference between the actual heat of combustion and the number calculated in accordance with the additive rule.

CHAPTER XI

CHEMICAL KINETICS

General.—Thermochemistry is dominated by the First Law of Energetics: it deals with the total amount of energy which accompanies chemical processes, and measures it in terms of heat. It is assumed that the processes actually take place to completion in the manner represented by the formulæ. The questions as to why the processes take place in the one direction instead of in the other, which is quite as possible from the mere formula, or whether the reactions are really as complete as they are tacitly assumed to be, are not taken into consideration at all.

It was at one time thought possible to answer these questions from the thermochemical data, with the aid of the rule that, of the two chemical reactions in contrary directions, the one which evolved heat alone took place. Since a change of energy takes place in chemical processes every chemical equation when read in one direction corresponds to an evolution of heat, and to an absorption of heat in the other direction.

This view, which has found support in very recent times, is not correct when expressed in this form.[1] It is the last residue of a doctrine first propounded by T. Bergmann in the last quarter of the eighteenth century. According to it chemical substances behave towards each other as mechanical masses under the influence of opposed forces; one or other force is the stronger, and the process takes place accordingly. As Bergmann regarded these "chemical forces" as conditioned solely by the nature of the substances and by the temperature, he was bound to assume that they were in action as long as any of the reacting substances were present, *i.e.* that the processes were all complete.

Although this view was in agreement with the knowledge of that time, only (practically) complete reactions being known or taken into account, closer observation revealed the fact that incomplete reactions, which according to the theory were impossible, were of

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[1] The rule would be correct at absolute zero, at which temperature both heat and volume energy disappear.

more frequent occurrence than was supposed. Accordingly C. L. Berthollet about the beginning of last century developed a theory embodying the opposite view. The fundamental idea of it was that the course of a chemical reaction is affected not only by the nature of the substances and by the temperature, but also by the amount of each substance present. Since the reacting substances disappear during the reaction, and the products of the reaction accumulate, the reaction will be hindered and will finally be stopped, because the resulting substances will tend more and more, as they accumulate, to regenerate the original substances. In consequence of this, the reaction will cease before it is complete.

Many reactions do proceed to completion, so far as can be ascertained experimentally, but the explanation is that, for some reason, accumulation of the products of reaction is prevented. If one of the products is a gas, it will escape and lose its effect; an insoluble product will separate out and be equally without further action.

These views have since received full confirmation, but a long time elapsed before Guldberg and Waage (1867) elaborated them into a real theory of chemical reaction and equilibrium. After the validity of Berthollet's views had been confirmed in many cases by later investigations, the development of energetics and the application of it to chemical problems gave rise to a system of "chemical dynamics" in which, notwithstanding the extraordinary extension of the subject, are still found the essential principles of Berthollet's doctrine of affinity.

The law of chemical mass action is the foundation of this development; according to it the chemical action is proportional to the active mass, *i.e.* to the concentration, or the quantity of substance in unit volume. The chemical action here spoken of may be exerted in two directions: in regulating the course of the action, and in regulating the equilibrium at the conclusion of the reaction. There are thus two divisions of the subject: chemical kinetics and chemical statics.

In a sense kinetics may be considered the fundamental science, seeing that the reaction must proceed before equilibrium can be established. But it is much less advanced than is statics. One reason for this undoubtedly is, that, owing to the time relation, it contains one variable more than does statics, and is correspondingly more difficult. Again, no general principle has been discovered as a guide in this region, like those guiding principles of equilibrium, based on the generalisation of the second law of thermodynamics. The importance of kinetics is sure to increase, for it affords more information regarding the nature of chemical systems than does chemical statics, and, further, indications are not wanting that the general principle will be forthcoming at no distant time.

Chemical Kinetics.—When C. F. Wenzel in 1777 set himself to the task of investigating the cause of chemical processes, or the laws of chemical affinity, he had first of all to search for a method of measurement. From analogy to the method adopted for measuring the causes of mechanical processes or of motion, he chose to measure chemical forces by the velocities with which they effected analogous processes.

The conception of "chemical velocity" is defined as the ratio of the amount of substance transformed in the process under consideration to the time required for its transformation. For example, the expression that fermentation proceeds faster at a high temperature than at a low one means that *cæteris paribus* more sugar is converted in a given time into alcohol and carbonic acid at a high temperature than at a low temperature. This chemical velocity has little more than an external similarity to mechanical velocity, and we must therefore be careful not to look upon the similarity as going deeper.

The quantity of substance decomposed in unit time—the rate or velocity of a chemical reaction—is obviously dependent on very many separate circumstances. Wenzel, who wished to measure the affinity of acids for metals, performed his experiments so that the surfaces of the pieces of metal which he exposed to the action of acids were of equal size, for he reasoned that the metal dissolved in a given time must be proportional to its exposed surface. He also saw clearly that the action of his dilute acids would vary with their concentration, the action being in fact proportional to the concentration, "for if an acid liquid dissolve a drachm of copper or of zinc in an hour, a liquid half as strong will require two hours to effect the same, provided that the surfaces and the heats be equal in the two cases."

The principle thus enounced by Wenzel, that the action is proportional to the concentration of the active substance, is in reality the fundamental principle of chemical dynamics. Berthollet stated it later and independently of Wenzel, but it is only quite recently that it has experienced the application to the measurement of "chemical forces" foreseen by the latter.

In the first place, it is clear that one of the complications of Wenzel's experiments may be avoided by relinquishing the employment of solid substances. Chemical processes may be instituted in homogeneous liquids and gases, where there is no question of surface at all. It is true that here the course of the processes is not always easy to follow and measure, but still in many cases this is practicable.

The Law of the Velocity of Reaction.—The first of such measurements was made in 1850 by Wilhelmy, who correctly stated the law of the progress of the simplest class of chemical reactions. If only one substance is affected in the process within a homogeneous fluid, it is manifest from the law of mass action that the velocity cannot remain constant, but must continually decrease; for supposing one-tenth of the substance present to be transformed in unit time, we should get a table like the following to show the course of the reaction:

Time.	Substance present.	Substance transformed.
0—1	1·000	·100
1—2	·900	·090
2—3	·810	·081
3—4	·729	·073
4—5	·656	·066

At the commencement the amount 1·000 is present, and after the lapse of unit time ·100 has been transformed according to our assumption. The amount ·900 is now left, of which a tenth, this time ·090, again undergoes transformation. The quantity remaining behind is now $\cdot 900 - \cdot 090 = \cdot 810$, of which again a tenth or ·081 is transformed, and so on.

If we denote by C the concentration of the substance at the time θ, and by dC the change[1] of concentration in the small interval of time $d\theta$, the law that the velocity of reaction is proportional to the concentration is expressed by the equation

$$-dC/d\theta = kC,$$

in which $-dC/d\theta$ is the velocity of reaction, or the ratio of the amount transformed to the corresponding time of transformation. The sign is negative, because the concentration decreases during the reaction, while the time increases. The meaning of k becomes clear, if C is put equal to 1; k is the velocity of reaction for unit concentration.

Finite Intervals of Time.—This equation cannot be tested directly by experiment. The concentration C changes continuously during the time $d\theta$. On the right side of the equation, therefore, a mean between the initial and final values of C during $d\theta$ must be inserted; but it is not apparent from the equation how this is to be calculated.

Obviously, less error is introduced by substituting the arithmetical mean of the initial and final concentrations for this unknown mean value, the shorter the interval of time $d\theta$ is made. If $d\theta$ is very small, the two concentrations are practically the same, and the uncertainty regarding the mean disappears altogether.

To test the equation, we must measure the very small changes of concentration and the corresponding times. These small differences of large numbers are very uncertain, the error being relatively larger the smaller the differences are. The two conditions are contradictory: very small differences if the formula is to hold, very large differences to avoid experimental error.

The formula cannot be accurately tested in this way. But the

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[1] As before d denotes a small change of the magnitude which follows.

changes which have taken place during a finite time θ, can be calculated from the formula which holds for very small times $d\theta$. For this purpose the time must be divided into a very large number of small parts $d\theta$, the change dC calculated for each portion of time, and these amounts added together.

This can easily be done with the aid of the Integral calculus, but a knowledge of this is not assumed here. To give some idea of the method, the calculation will be gone through, for which purpose we will substitute a general expression for the arbitrary fraction employed on the table on p. 289. Putting the fraction transformed in unit time equal to k, and the original amount equal to 1, we obtain

Time.	Substance present.	Substance transformed in unit time.
0—1	1	k
1—2	$1-k$	$(1-k)k$
2—3	$1-k-(1-k)k=(1-k)^2$	$(1-k)^2k$
3—4	$(1-k)^2-(1-k)^2k=(1-k)^3$	$(1-k)^3k$
4—5	$(1-k)^3-(1-k)^3k=(1-k)^4$	$(1-k)^4k$

If we therefore denote by θ the interval from the commencement of the reaction, the amount of substance still present at the time θ is $(1-k)^\theta$. This holds if the initial concentration is 1; if it is C_0, the concentration C at the time θ is

$$C/C_0=(1-k)^\theta \text{ or } C=C_0(1-k)^\theta.$$

The equation, however, has been deduced on an inexact assumption. We have conceived the process as if the transformation took place in the consecutive units of time at a uniform velocity, and changed suddenly at the beginning of the next unit, corresponding to the diminished amount of substance present. Now this is not what really occurs, for the change evidently proceeds continuously; we can, however, approximate closely to the actual process by choosing the units of time as small as possible.

If we introduce a unit of time which is n times smaller, the amount transformed in unit time is k/n, while the number of units of time has risen to $n\theta$. For the same moment of time we have $C/C_0=(1-k/n)^{n\theta}$, instead of the less accurate equation $C/C_0=(1-k)^\theta$.

The greater n becomes the more accurate is the equation, and it will be exact when $n=\infty$. Then $k/n=0$, and the expression becomes $(1-0)^\infty$. From higher mathematics we learn that in this case the expression $(1-k/n)^{n\theta}$ becomes equal to $e^{-k\theta}$, where e is the basis of the natural logarithms, 2·7183.

Accordingly, we have $C/C_0=e^{-k\theta}$, or $C_0/C=e^{k\theta}$, or, if we take the logarithm to the base e of both sides,

$$\lg C_0-\lg C=k\theta,$$

which is the desired expression of the law connecting the time θ with the concentration C at that time.

The mathematical expression of the law of mass action leads to the following finite equation:

$$\lg C_0 - \lg C = k\theta,$$

in which C_0 is the initial concentration, C the concentration at the time θ, and k is the velocity constant: the definition of the latter is contained in the deduction of the equation; it is the fraction of the original substance which would be transformed in unit time, if the initial velocity remained constant during unit time.[1]

Units.—The unit of concentration is the unit amount in unit volume. The chemical unit is the mol, or if this is not known, the formula-weight in grams. The cubic centimetre is the absolute unit of volume, but in this unit concentrations are represented by very small numbers; it is therefore customary to take the litre as unit of volume, and unit concentration is one mol in a litre.

The time should be measured in seconds, but the minute has been adopted as the unit in chemical kinetics; it may be retained for the present, as no certain relation between velocity of reaction and other magnitudes which are measured in absolute units is known as yet.

Finally, common decimal logarithms may be substituted for the inconvenient natural logarithms. The relation is $\log C = {\cdot}4343 \lg C$, and the equation becomes:

$$\log C - \log C_0 = {\cdot}4343\ k\theta,$$

which is the form in which it is usually applied.

A glance at the equation shows that the value of the constant k is independent of the unit of concentration. If the unit is made n times smaller, the numbers become n times larger, but the left side of the equation $\log nC - \log nC_0$ remains equal to $\log C - \log C_0$. Any unit of concentration may therefore be used in the calculation.

The value of the constant is independent of the unit of concentration only in this the simplest type of velocity of reaction; in all other types change of unit alters the value of the constant, as will be shown later.

Example.—Wilhelmy first showed the validity of this formula in the case of the inversion of cane-sugar, which decomposes under the influence of free acid into glucose and fructose, taking up the elements of water, thus: $C_{12}H_{22}O_{11} + H_2O = 2C_6H_{12}O_6$. Here the acid suffers no change, and the water in such experiments is always present in so great excess that the alteration of its quantity is quite inappreciable. The conditions for the deduction of the equation are therefore fulfilled. In order to determine the quantity of unchanged cane-sugar present at any time, he took advantage of the rotation of the plane of polarisation by the sugars, which thus enabled him to

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[1] This definition of k is only different in form from that given on p. 289.

perform the analysis without any chemical disturbance of the state of the system. He obtained, for example, the following series of numbers:

θ (Minutes).	Angle.	Concentration.	$\log C_0 - \log C$.	·4343 k.
0	46·75°	65·45	...	...
15	43·75°	62·45	·0204	·00136
30	41·00°	59·70	·0399	·00133
45	38·25°	56·95	·0605	·00134
60	35·75°	54·45	·0799	·00133
75	33·25°	51·95	·1003	·00134
90	30·75°	49·45	·1217	·00135
105	28·25°	46·95	·1441	·00137
120	26·00°	44·70	·1655	·00137
∞	− 18·70°	...	...	...

Mean ·4343 k = ·00135, whence k = ·00310.

The observations are calculated as follows: The original sugar-solution had the rotation 46·75°; after it had been completely converted into glucose and fructose its rotation was − 18·70°. As the rotation is proportional to the quantity of sugar present, the total angle traversed, viz. 46·75° + 18·70° = 65·45°, is the measure of the total amount of sugar. The angle after the expiry of 15′ is 43·75°, from which C is 43·75 + 18·70 = 62·45. The difference between the logarithms of the two numbers is equal to ·0204, and this divided by $\theta = 15$, the number of minutes from the commencement, gives ·00136. $\frac{1}{\theta}(\log C_0 - \log C)$, given in the last column, is, according to the equation, equal to ·4343 k, and must therefore be constant. As we see from the table, this is actually the case; for the slight variations are merely due to the errors of experiment.

The following table contains the results of the same experiment calculated from the formula $-dC/d\theta = kC$; the intervals of 15 minutes between consecutive readings are taken as $d\theta$, dC is the corresponding change of angle, and the mean of the initial and final values for these times is taken as C.

$d\theta$	$-dC$	C	k
15	3·00	63·95	·00312
15	2·75	61·08	·00300
15	2·75	58·33	·00315
15	2·50	55·70	·00300
15	2·50	53·20	·00313
15	2·50	50·70	·00328
15	2·50	48·20	·00335
15	2·25	45·83	·00328
		Mean k	·00316

It is seen that the individual numbers vary more than when the other formula is used, and that the average is almost two per cent higher. Still the results obtained in this manner are always a tolerable approximation, especially in the present case, where the angles could not be measured to less than ·25°, and each value of dC may be inaccurate to ± 4 or 6 per cent.

Other Applications of the Equation.—Results similar to those obtained by Wilhelmy for the inversion of cane-sugar have appeared later in the investigation of a great number of other chemical processes. For example, the reduction of permanganate ion by a great excess of oxalic acid, the hydrolysis of a dilute aqueous solution of methyl acetate into methyl alcohol and acetic acid in presence of acids, the conversion of dibromosuccinic acid into hydrobromic acid and bromomaleïc acid, of monochloracetic acid into glycollic acid, the transformation of atropin into hyoscyamin by alkalies—all these proceed according to the same law, which in no way depends on the substances taking part in the reaction: whenever a chemical process takes place, so that the amount of one substance only is changed, it proceeds according to the formula $\lg C_0 - \lg C = k\theta$. This, again, is merely a mathematical deduction from the principle that the chemical action is proportional to the active mass or concentration.

Theoretically, as the equation shows, a reaction never can come to an end. For, however great the time may be, $\log C_0 - \log C$ still has a finite value, *i.e.* there is still some undecomposed substance present. Only when $\theta = \infty$ does $\log C_0 - \log C$ become infinite or $C = 0$.

This theoretical deduction cannot be experimentally verified, because all methods of determination are limited and when the concentration C has fallen below a certain value, it cannot be determined at all, and is not recognisably different from zero. The limit of ordinary methods of analysis may be placed at ·001 of the original amount; so soon as the initial concentration has fallen below this, zero has been practically reached. A simple calculation, which may be left to the reader, shows that after a period ten times as long as the time required for the transformation of half the substance, the concentration is less than ·001 of the initial concentration, and the end of the reaction has been reached.

It should be stated at once that other reactions, which do not follow the laws developed above, also theoretically require infinite time to come to an end. The ratio between the time required for half and for ·999 to be transformed, is so different in the other cases that the rule does not apply.

Reaction of the Second Order.—We come to a second kind of chemical process, regulated by a new law, when in its course two substances undergo change of quantity. We must again assume that the action is proportional to the concentration of each present. From this it follows that the action is proportional to the product of the two concentrations; for this is the only function that fulfils the condition.

At first sight two equations seem to be required to express such a reaction, since two substances change in concentration at the same time. But the one change is not independent of the other, the two being proportional to each other; and if the chemical equation is given, the state is completely defined by a single variable.

Let us consider first the case in which an equal number of mols of the two substances react together; the simultaneous change in concentration of the two substances is the same and can be denoted by the same expression, dC. Accordingly the fundamental equation for this kind of reaction, known as reactions of the second order, is

$$-dC/d\theta = kCC',$$

where C and C′ are the molar concentrations of the two substances. By k is again denoted the velocity-coefficient, *i.e.* the velocity of the reaction if the concentration of both reagents was maintained at unity.

Here, again, in order to test the law, it is necessary to pass from the equation which holds for infinitely small intervals of time (the differential equation) to an expression which represents the transformation accomplished in any finite interval of time. The elementary calculation of this equation (the integral equation) is so tedious and unconvincing that the result (which is immediately obtained by means of the integral calculus) only is given. Two different formulæ are obtained depending on whether the initial concentrations are the same (*i.e.* equi-molar) or different.

If the initial concentrations C_0 and C_0' are the same, they remain so throughout the reaction, and the integral equation is

$$1/C - 1/C_0 = k\theta,$$

in which C is the common concentration at the end of the time θ.

An example of such a process is to be found in the saponification of ethyl acetate, investigated by R. Warder (1881).

θ	C	$\frac{1}{C}-\frac{1}{C_0}$	k
0	16·00	...	...
5	10·24	·563	·113
15	6·13	1·601	·107
25	4·32	2·705	·108
35	3·41	3·69	·106
55	2·31	6·94	·108
120	1·10	13·55	·113

In the last column we have the values of $\frac{1}{\theta}\left(\frac{1}{C}-\frac{1}{C_0}\right) = k$, which, according to theory, ought to be constant. In this case also the slight deviations only arise from experimental errors.

What was said with regard to processes of the first kind applies equally to processes of the second. The constant k is determined only by the nature of the substances present, the temperature, and the concentration; if we know its value, the whole course of the reaction is fully specified.

When the two reacting substances are not present in the same concentration, the equation is somewhat more complicated, and still more unsatisfactory to deduce in an elementary manner. The result is, if the two concentrations are denoted by C_0 and C_0',

$$\lg \frac{C_0'C}{C_0C'} = (C_0 - C_0')\, k\theta,$$

where lg is the natural logarithm, C and C′ the concentrations of the two substances at the same instant, after the interval of time θ. This equation also has been tested and found to agree with experiment.

Reactions of Higher Order.—We must now consider reactions in which three substances take part. The considerations put forward in the case of reactions of the second order apply here too, the fundamental equation being

$$-dC/d\theta = KCC'C'',$$

in which C, C′ and C″ are the concentrations of the three reagents.

This equation can be integrated for finite times, the form obtained varies with the equality or difference of the three initial concentrations. They may be omitted here for the reason that reactions of the third order seem to occur very seldom; so seldom, indeed, that only after prolonged search were such reactions discovered at all.

Reactions of the fourth order, in which four different substances interact at the same time, have been discovered and investigated in very small number only.

Investigations of reactions of higher order have shown that many reactions which, from the chemical equation, ought to be of higher order, are nevertheless of lower order. The cause of this seems to be that the reaction does not actually take place as represented by the ordinary chemical equation, which expresses the final result of a series of consecutive partial processes, and that these processes may be of a lower order than that of the final equation.

Such investigations afford evidence of the existence of these intermediate reactions, and in this way deepen our insight into the nature of reactions.

Incomplete Reactions.—In all this discussion the assumption is made that the processes, the course of which is represented by the equations, are complete and that the products do not react with formation of the original substances. As already stated, this is never strictly accurate, and the possibility that the reverse action really takes place in every case must be admitted. A solution of glucose and fructose, for example, in presence of acid must produce a certain, in all probability extremely small, amount of cane sugar. The equations developed without taking account of this possibility represent the experimental results within the limits of error, because in very many cases the amount of the reverse action is less than the experimental error, and is therefore unrecognisable. Within these limits the equations are correct, although theoretically there is a certain degree of error.

There are, however, many processes in which the reverse action assumes considerable proportions, neglect of which introduces correspondingly large errors. The deduction of the equation for such a case is as follows.

If a substance A_1 changes into another substance A_2, and conversely, the velocity of the former transformation is proportional to the concentration of A_1, and of the latter transformation to the concentration of A_2; the equations for these reactions, if C_1 and C_2 are the corresponding concentrations, are $-dC_1/d\theta = k_1C_1$, and $-dC_2/d\theta = k_2C_2$.

We apply the principle of coexistence to the simultaneous course of these two processes, *i.e.* we assume each of the two opposed reactions to follow the law of mass-action, as if the other were nonpresent, except for the change in concentration caused by the other substances. The actual change of concentration dC is the difference of the two partial changes $dC = dC_1 - dC_2$, since the substance is formed by the one process, and destroyed by the other. Introducing these values from the two single equations we have:

$$-dC/d\theta = k_1C_1 - k_2C_2.$$

This equation can be treated in the same manner as the equation for a simple reaction of the first order (p. 290), and has been experimentally verified.

The equation for a reversible reaction of the second order is obtained in a similar manner:

$$-dC/d\theta = kC_1C_2 - k'C_1'C_2',$$

where C_1 and C_2 refer to the original substances, C_1' and C_2' to the products of the reaction. These four values are connected by the chemical equation, so that if the four concentrations are given for one definite instant of time, they are all fixed for any other time, when the value of any one of them is known. For dC_1 must $= dC_2$, $dC_1' = dC_2'$, and $dC_1 = -dC_1'$; and if the single equations are set down, and added up in accordance with the principle of coexistence, the above equation is obtained at once.

This complicated equation has been tested in several cases, and has been found to agree with experiment.

This does not by any means exhaust the possible kinds of compound reactions. There is no need to proceed further, as all of them can be treated by means of the principle of coexistence, and can be solved, theoretically at least.

Reactions between two Phases. — We have still to take up reactions in heterogeneous systems, or, in other words, between two phases. There is an interface between the two phases, and in it the reaction takes place. The fundamental law was put forward by Wenzel: the amounts transformed are proportional to the size of the surface of contact. The velocity of reaction also depends, according to the law of mass-action, on the concentrations of the reagents in the interface. As a rule the distribution of the concentrations in the single phases is not uniform, and the velocity then depends on the manner in which (by diffusion, convection, etc.) the concentrations in the interface are regulated.

In some of the simpler cases the fundamental law, that the amount transformed is, *cæteris paribus*, proportional to the surface of contact, has been experimentally confirmed. The numerous changes of concentration in the interface, brought about by the reaction, frequently introduce such complications that theoretical treatment becomes very difficult.

Effect of Temperature.—In conclusion, some observations will be made on the constants obtained in these investigations. Under fixed conditions of substances (including solvent, if any), of temperature and of pressure, velocity coefficients are real natural constants, as much as are any other magnitudes which can be measured and reproduced. They may therefore be used for the recognition of substances,[1] and even for their quantitative estimation, provided the law of mass-action holds good.

Increase of temperature almost always increases the velocity considerably. There are very few other magnitudes which are affected to anything like the same extent.[2]

The effect varies to a slight extent with the nature of the reaction; on the average, a rise of temperature of 10° doubles the velocity.

Pressure, on the other hand, has a very small effect, large pressures being required to cause a measurable difference.

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[1] Later, in dealing with Radioactivity, we shall come across substances about which practically nothing is known except their velocity constants.

[2] Vapour pressures show a similarly large alteration, amounting to almost a numerical approximation. This does not seem to be a mere coincidence, for the active mass of liquids is measured by their vapour pressure (as will be seen from considerations advanced later on), and the velocity of reaction is proportional to the active mass; some such connexion was only to be expected. But in addition to this there is the specific effect of temperature on the velocity.

It should also be noted, that the velocity of reaction in gaseous systems also changes to about the same extent, and this relation cannot apply to them.

Catalysis.—The presence of "foreign" substances, *i.e.* which do not appear in the chemical equation, has always some effect. In many cases they have very little effect on the velocity, but in others it is very large; in some instances the merest trace of a foreign substance will increase the velocity enormously, or reduce it to a small fraction. Substances which have a marked influence on the velocity are called catalytic agents or catalysers. The differences are purely quantitative (though they may be extremely great); in theory every foreign substance acts catalytically, *i.e.* changes the velocity.

There are very great differences among the velocity constants, embracing the whole region of measureable and observable values. The quickest reactions are those between ions in aqueous solutions: the velocity exceeds our present limits of measurement. Reactions between organic compounds are usually slow; hence the frequent recourse to high temperatures in closed vessels.[1] Most reactions between gases, except those at high temperatures, are also very slow. If the reactions are technically important, suitable catalysers are employed, in order to increase the velocity to a sufficient extent. The velocity of metabolic changes in plants and animals is regulated by catalysers of widely different kinds. On this account catalytic actions are of extraordinary importance, and a knowledge of their general laws will have an incalculable influence on technical chemistry, no less than on Physiology and Medicine.

The Laws of Catalytic Phenomena.—Scientifically, catalysis is not very far advanced, for, in spite of its importance, and of the fact that it has been known for over a century, it has only been systematically studied in recent years. The reason is that no suitable conception of catalysis was possible before the development of the doctrine of reaction-velocity, seeing that catalysis consists in changing the velocity of chemical reactions by the presence of substances which do not appear in the final products of the reaction.

As to the laws of catalysis, it must first be said that it is a very general phenomenon. There is probably no reaction unaffected by some catalysers, and no substance which does not catalytically affect some reaction. But no general relation has been discovered between the kind of reaction and the kind of catalyser. It may be remarked that substances capable of undergoing reversible chemical transformations frequently catalyse reactions which are similar to these reversible actions. Thus, elements giving rise to several oxidation products which are easily changed into each other, are frequently oxidation catalysers, and the corresponding chlorides, or

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[1] The assumption occasionally made, that the pressure has a great effect, is erroneous. Pressure is only necessary to keep the substances liquid at temperatures which are sufficiently high to effect a large increase in the velocity of reaction.

the elements themselves, accelerate the process of chlorination. This description covers only a part of the known cases.

But these cases have suggested a theory of catalysis which has turned out to be in the main correct, at least in many cases. It consists in the assumption of intermediate reactions of the following kind. Let A and B be two substances which interact very slowly with formation of AB; a foreign substance K is now added, which reacts quickly with B forming KB; KB is also rapidly decomposed by A in such a manner that AB and K are formed. The process can now be repeated, and will continue until A or B is exhausted, since the catalyser K suffers no loss.

The first example of catalysis explained in this way (before the conception and the name were known) was the formation of sulphuric acid by the chamber process from sulphur dioxide, water vapour and oxygen with the aid of oxides of nitrogen. In a masterly research Clément and Desormes (1806) showed that the reaction between sulphur dioxide and oxygen is very slow, while the former is very rapidly oxidised by nitrogen peroxide, and the resulting nitric oxide is also very rapidly converted by oxygen into the peroxide. Thus the final result of the process is the same as a direct oxidation of sulphur dioxide; but the process takes much less time, and the catalyser is not used up, as it does not appear in the final product, sulphuric acid.

It seems at first sight improbable that an indirect road, viz. that the oxygen first unites with nitric oxide and then goes from it to the sulphur dioxide, can lead more quickly to the goal than the direct union. Still it does happen so, and it is the task of science to bring it into harmony with other known facts. It has been stated already that no connexion is known between the energy and the absolute velocity of a reaction, such as, for example, that processes in which there is the greatest loss of total energy or of free energy, have the greatest velocities. Rather they seem to be quite free in this respect, and the factors which do regulate them are unknown. It is, therefore, no objection to the theory of intermediate reactions that the two stages of the indirect method have smaller differences of energy than the direct reaction. It should rather be a stimulus to renewed effort to discover the general law, up to the present unknown, connecting the chemical nature of a reaction with its velocity; more especially so, as we should then be in a position to predict theoretically these catalysers, instead of empirically seeking for them, as at present.

It is difficult to decide whether all cases of catalysis can be reduced to this category, but it does not seem at all probable. Hydrion, for instance, has a very strong catalytic action in many widely different cases, in which the assumption of intermediate reactions is not in accordance with our present knowledge.

Most catalysers have a marked individual character; in other words it is impossible to arrange catalytic effects in groups in which the same components have the same acceleration factor. The only comprehensive rule is that in homogeneous systems, liquids in particular, the acceleration is proportional to the concentration of the catalyser, but only for small concentrations. The inversion of cane sugar by hydrion under the same conditions is so closely proportional to the concentration, that the velocity of the reaction is a very convenient method of determining the concentration.

Catalytic Retardation.—The answer to the question as to the existence of retarding catalysers, in addition to accelerating catalysers, is that there certainly are substances, the addition of which markedly decreases the velocity of reaction. Such cases are comparatively few, and in one case, which has been carefully investigated, the retardation is a secondary effect, due to the inactivation of a catalyser which was present. This case is the oxidation of sulphites by free oxygen, which is very strongly retarded by many organic substances, such as alcohol, mannite, etc. It has been found out that extraordinarily small traces of copper ion, far below the concentration recognisable by ordinary analytical methods, are present in all ordinary solutions, and cause the comparatively rapid oxidation, and that the retarding catalysers convert copper ion into inactive complex compounds, so that the reaction proceeds at its natural rate. Although this does not prove all catalytic retardations to be caused in this way, it is necessary to examine any case of retardation very closely before concluding that directly retarding catalysers exist at all.

Reversible Reactions.—Catalytic actions are known both in one-phase systems, gases and liquids, and in heterogeneous systems. To the former belongs the inversion of cane sugar by acids, *i.e.* by hydrion. It may be remarked that almost all hydrolytic processes, *i.e.* decompositions with addition of the elements of water, are accelerated by hydrion. The same is true for the reverse processes: condensations with loss of the elements of water. In general a catalyser which accelerates a given process, must accelerate the reverse process to the same extent. The equilibrium is practically unaffected by the catalyser, so long as its concentration is very small in comparison with the amounts of the reagents, since the equilibrium is fixed by the energy relations, and can only be disturbed by the expenditure of energy, which the catalyser cannot as a rule supply. Since, further, equilibrium is the state in which the opposing reactions have the same velocity, a catalyser, if it accelerates the one reaction, must also accelerate the other in the same ratio. It has been experimentally shown that the addition of a catalyser does not generally displace the equilibrium, even when it acts as a very powerful accelerator, and that the acceleration of the reverse reaction is equally great.

Heterogeneous Systems.—The acceleration of oxidations by means of platinum and the allied metals is a well-known example of heterogeneous catalysis. So far back as the beginning of last century Döbereiner discovered the ignition of hydrogen in air by means of spongy platinum, and based on it his lamp, which has been revived in the modern automatic gas-lighter, which likewise depends on the action of spongy platinum. The catalytic acceleration of the oxidation of sulphur dioxide in air has recently become of technical importance in the manufacture of sulphur trioxide, platinum sponge, iron oxide, or other solid catalyser being employed for the purpose.

Enzymes.—The action of organic ferments and enzymes is catalytic. Almost all the important physiological processes, such as assimilation in plants, digestion in animals, and the oxidation of products in the tissues, depend on the catalytic action of certain substances, whose chemical nature is as yet almost unknown. In many respects they resemble albumins, and all lose their activity in aqueous solution at fairly low temperatures, between 60° and 100°. This is one reason why life is destroyed at these temperatures, for the vital chemical functions cannot be performed without these catalysers or enzymes. They differ exceedingly in other respects, and exercise the most diverse analytical and synthetic functions in the organism. The primitive arts of bread-making, brewing, cheese-making, etc., all depend on the action of the enzymes occurring in small organisms, the presence or increase of which brings about the particular processes of these arts.

Autocatalysis.—It frequently happens that substances, produced or used up during a chemical reaction, act catalytically on the course of the reaction; in such cases we have autocatalysis. The most striking type of autocatalytic actions is that in which an accelerator is formed during a naturally slow reaction. In this case, a long time elapses after the substances are mixed, before the process begins "to go," *i.e.* proceeds with appreciable velocity. When it has once begun, the increasing concentration of the catalyser makes it faster still, as this effect more than balances the diminution caused by the using up of the substances. As soon as these two opposite effects

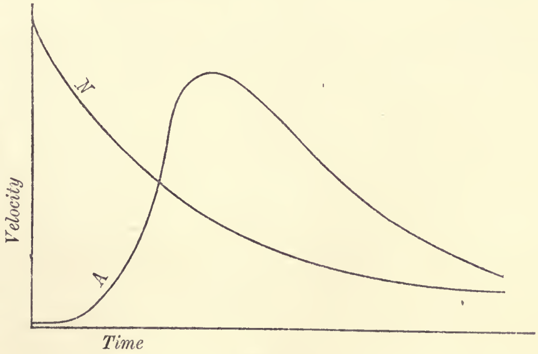

FIG. 35.

become equal, the velocity reaches its maximum, and after this falls off, since, when the reagents are exhausted, the velocity must fall to zero. This is quite different from ordinary chemical reactions, in which the concentration of the active substances is greatest at the beginning and steadily falls off during the reaction, the velocity following the same course. In Fig. 35 N shows the normal course of the velocity with the time, while A represents the velocity of an autocatalytically accelerated reaction.

An example of such processes is the dissolution of a metal, *e.g.* silver or copper, in nitric acid. In pure nitric acid the reaction is extremely slow, but is very quick if the acid contains lower oxides of nitrogen, which act as accelerators. If the metal is placed in pure acid, it remains almost unacted on at first, but as the solution becomes richer in oxides of nitrogen as the metal dissolves, the process goes on more rapidly until it becomes violent. When the acid is used up, the reaction under any circumstances finally quietens down.[1]

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[1] The heating of the solution by the heat liberated during the reaction acts in precisely the same way as autocatalysis, and induces (together with it) explosive reactions. Still the processes described above occur when suitable means are taken to keep the temperature constant.

CHAPTER XII

CHEMICAL EQUILIBRIUM OF THE FIRST ORDER

General.—The law of mass-action governs two groups of phenomena, as has already been stated: the course of the reaction with time, and the equilibrium to which this leads. Both obey the general law that the tendency of a substance to undergo transformation increases with its concentration. Accordingly, the tendency of a substance to be formed during a reaction is inversely proportional to its concentration.

In any chemical reaction the decrease in amount of the original substances will diminish their tendency to undergo transformation and also the velocity, while the increase in the amount of products of the reaction will increase their tendency to reunite, and the velocity with which the reunion will take place. The final result will be that these two tendencies neutralise each other, and the reaction will come to a standstill.

The same considerations apply if the reaction takes place in the reverse direction. If the external conditions, such as pressure, temperature and concentration, are the same in the two cases, the transformation must stop in both at the same proportion of initial substances to products. This state is known as a chemical equilibrium, after the analogy with mechanical equilibrium.

It is characteristic of stable mechanical equilibrium in the widest sense that a displacement of the state originates effects which resist the displacement, and tend to restore the initial state. The same definition applies equally well to chemical equilibrium. The effect produced is an alteration in the relative amounts of the reagents. There is a fixed ratio for which the system is at rest; if this ratio is changed, a chemical action takes place, the tendency of which is to restore the previous ratio.

It comes to the same thing, if we represent chemical equilibrium as a state in which the velocity of the reaction and of the reverse action are equal. Since the velocities depend on the concentrations, the two velocities can be equal, or the total velocity be zero, only for a fixed ratio of the concentrations.

Irreversible Reactions.—When these general considerations are compared with common experience of most chemical reactions, there is found to be only a partial agreement between them. No doubt, many such equilibrium states are known, but there are many more in which no equilibrium is apparent, and which convey the impression of being one-sided: only one of the two opposed reactions takes place, there being no evidence of the other.

Thus hydrochloric acid appears to react completely with sodium hydroxide with formation of sodium chloride and water; the reverse reaction, the decomposition of sodium chloride by water into hydrochloric acid and sodium hydroxide, appears to be impossible. Nevertheless, in the very similar reactions, in which ammonia takes the place of sodium hydroxide, or carbonic acid that of hydrochloric acid, the reverse action is observable: in the first case the solution is slightly acid, a sign that a little of the hydrochloric acid is uncombined, and in the second it is strongly alkaline, because normal sodium carbonate in water is decomposed to such an extent, that a marked amount of sodium hydroxide is formed. All the stages exist between salts which are certainly partially decomposed and those in which decomposition is not recognisable.

As a generalisation from this example we may state that, of the equilibria which really exist, we can only recognise the comparatively few cases in which the concentrations of all the substances participating in the equilibrium are recognisable by ordinary analytical methods. As these are always being extended, the region of equilibrium is also expanding, and, as no contradiction to the generalisation of equilibrium has as yet been found, we may regard it as an induction which is experimentally justified.

Apparent Equilibrium.—An important matter must be mentioned at once. The above considerations apply to real equilibrium, which, according to the definition given, is reproduced if the system has been disturbed. The velocity of this process varies very much and always becomes smaller in the vicinity of equilibrium. It may often happen that a system appears to remain unchanged with time, not that it is in equilibrium, but because its velocity of reaction is so small that the change eludes observation. The difference between these states and true equilibrium is easily recognised, for they are not attainable from either side in measurable time, and accordingly, they are not re-established automatically after displacement has been produced.

In mechanics we have stable, indifferent and labile equilibrium; the above definition only applies to the first. Labile equilibrium is a mathematical fiction, since the complete absence of disturbances, on which the existence of labile equilibrium depends, cannot be attained. It is inappropriate to call the state of overcooling, etc. (p. 67), labile, and to do so leads to misunderstanding.

On the other hand, labile states in a chemical sense are those which are inherently unstable, and pass into other states without any external interference. As not a few chemical reactions proceed so slowly that the change is imperceptible, there are very many systems which are chemically labile, but seem to be stable within a finite time. As regards reactions which proceed rapidly, these pseudo-stable systems behave like ordinary stable systems.

There is, however, an analogy with mechanically indifferent equilibrium. In mechanics a system is said to be indifferent to changes of conditions which do not affect stable equilibrium. In chemical equilibrium the quantities of the different heterogeneous phases come under this heading. A simple example is the equilibrium between a liquid and its vapour; this is absolutely independent of the absolute or relative amounts of the two phases: the system is in indifferent equilibrium with respect to alteration of these amounts.

The Order of Equilibrium.—The various cases of chemical equilibrium can be classified in accordance with the number of components participating in the equilibrium. Equilibrium of the first order, in which there is only one component, has been already dealt with in part, in connexion with the changes of the state of aggregation, with which were included allotropic and polymorphous transformations. The former are often called physical equilibria, in contrast with chemical equilibria. This distinction is superficial and has no natural basis, for the laws of chemical equilibrium in the restricted sense are based on exactly the same principles as is physical equilibrium. There are other equilibria of the first order, as, for example, the dissociation of nitrogen peroxide, N_2O_4, into $2NO_2$, of iodine, $I_2 = 2I$, and many similar cases, which are admittedly chemical processes.

In equilibrium of the second order, there are two different substances or components; in it are included solutions, and many cases of chemical equilibrium in the stricter sense.

Components.—The components of a system in equilibrium are not necessarily its elements. The components are the substances by means of which the composition of all the phases concerned in the equilibrium can be expressed. If all the phases have the same elementary composition (and can be changed into each other), there is only one component; if the composition of all the phases can be represented as the sum of appropriate amounts of two substances (it is immaterial whether they are present in the pure state or not), the equilibrium is of the second order; and so on. A solution of magnesium sulphate in water, along with solid salt and water vapour, is an equilibrium of the second order; for every phase can be represented by the formula $xMgSO_4 + yH_2O$, in which x and y can assume any value (including zero). (See p. 312.)

Degrees of Freedom.—A second method of classification is afforded by the Phase Rule (Gibbs, 1874). We have already seen (p. 60) that a pure substance, *i.e.* an equilibrium of the first order, has two degrees of freedom if it exists as a single phase, *i.e.* its state is not defined unless definite values are assigned to two magnitudes on which it depends. If a second phase is added (*e.g.* vapour to water), only one degree of freedom is left, and only one magnitude can be arbitrarily varied. On the addition of a third phase all the degrees of freedom are lost (p. 100).

If there is more than one component, the number of degrees of freedom increases with the number of components, one more for each component. If C is the number of components and P the number of phases in an equilibrium, the number of degrees of freedom F is given by the equation

$$F = C + 2 - P.$$

This comparatively simple formula is of very wide applicability, and leads to the most diverse conclusions, which are, however, qualitative only. By means of it, the disputed question whether solubility is affected by pressure can be settled at once. Let us consider a system consisting of the solid and the solution in equilibrium with it at any given pressure. The number of components is two, the number of phases is the same; there are two degrees of freedom, according to the formula. One of these is disposed of when we fix upon any given temperature; there remains one degree of freedom, and, in consequence, the composition of the solution must vary with the pressure; this has been demonstrated by actual experiment.

Equilibrium of the First Order.—In the section dealing with abnormal vapour densities (p. 165) several instances were given of gases, the properties of which change under the influence of temperature and pressure without any change in chemical composition. The earliest known example is nitrogen peroxide, the transformation being represented by the equation $N_2O_4 = 2NO_2$. This equation was based upon the change in molar weight obtained from the vapour density. But other changes are also connected with this. In particular, the vapours in the state represented by the first formula are only slightly coloured, and the colour becomes darker brown as the fraction of it in the form of NO_2 increases.

This change of colour can be employed to determine the ratio of the two fractions, on the probable assumption that the colour of the mixture is the sum of the colours of the components. More frequently, use has been made of the density determinations.

If the value of R in the gas equation $pv = RT$ is found for one mol of N_2O_4 or 92 g. of the substance, it is found to vary with the temperature and the pressure between the normal value and double the normal value, corresponding to the decomposition expressed by the above equation. If x is the fraction of undecomposed N_2O_4, the observed value of the constant, denoted by r, for the mixture will be $xR + 2(1 - x)R$, or $r = R(2 - x)$, whence $x = 2 - r/R$. If, therefore, $r = pv/T$ is determined for 92 g. of the (partially decomposed) mixture, the degree of decomposition can be found at once. Since, further, r and R are inversely proportional to d and D, the density of the partially decomposed mixture and of the undecomposed substance N_2O_4 respectively, the ratio r/R can be replaced by D/d, and the equation becomes $x = 2 - D/d$.

Experiments show that d is smaller the smaller the pressure, the decomposition increasing with decrease of pressure. The law for this effect of pressure can be deduced theoretically.

Direct application of the law of mass-action would in this case lead to the following equation. If we put the effect of each form of the peroxide on the equilibrium proportional to its concentration, the equation would be $a = kb$, in which a and b are the concentrations of N_2O_4 and of NO_2, and k is a coefficient which may vary with the temperature. This equation is not in agreement with experiment, for it leads to the conclusion that the ratio of the two concentrations is independent of their absolute value, whereas decrease of concentration (decreasing pressure) alters the ratio in favour of NO_2.

It can be seen in a general way, that in this case pressure must have some effect upon the degree of decomposition, since this has an effect upon the pressure, the pressure increasing when NO_2 is formed at the expense of N_2O_4. The volume effect must find expression in the equation. The only way of doing this, without contradiction of the assumptions made, and without introducing new coefficients, is to introduce powers of the concentrations. The equation

$$a = kb^2$$

completely represents the behaviour of nitrogen peroxide with varying concentration (or pressure) and constant temperature. It has been frequently tested and found to be in agreement with experiment.

In general, if one mol of a gas decomposes into n mols of another, and if a and b are the respective concentrations, the equilibrium equation for constant temperature, or the equilibrium isothermal, is given by the equation $a = kb^n$.

This formula indicates that the concentration affects the equilibrium only when n is not unity. If $n = 1$, the two concentrations remain proportional to each other; the degree of decomposition does not change if the mixture is subjected to a different pressure, because the two concentrations are changed in the same ratio. The equation further indicates that a change in the concentration b has a greater effect than the same change in a; for nitrogen peroxide, where $n = 2$, to double b will cause a to increase fourfold, if the equilibrium is to remain the same. Consequently, the decomposition must recede when the pressure is increased, or, in other words, that process takes place which opposes the increase of pressure by partially using it up.

Theoretical Deduction.—The above equation can be strictly deduced from the definition that a state of equilibrium occurs when for an infinitely small displacement of equilibrium the total amount of work is zero (p. 13). The work which a gas performs when expanding from v_1 to v_2 at constant temperature is $R T \lg(v_2/v_1)$ (p. 40), or, since $v_2/v_1 = p_1/p_2$ at constant temperature, $R T \lg(p_1/p_2)$ or $R T(\lg p_1 - \lg p_2)$. For small alterations of pressure p the work is, in the usual notation, $d(R T \lg p)$ or $R T\, d \lg p$.

If the equilibrium is displaced in the system under consideration, 2, or in general n, mols of B are produced when one mol of the original substance A disappears. The corresponding amounts of work are

$$n R T\, d \lg p_B \text{ and } R T\, d \lg p_A,$$

and their sum must be zero, according to the definition. We have $n R T\, d \lg p_B - R T\, d \lg p_A = 0$, or $n\, d \lg p_B - d \lg p_A = 0$, or $d(n \lg p_B) - d \lg p_A = 0$, or $d \lg p_B^n = d \lg p_A$. The simultaneous alterations of the logarithms of p_B^n and of p_A must be equal; this occurs when the two numbers are in a constant ratio, for then their logarithms differ by a constant number and their simultaneous alterations are equal. If this constant ratio is denoted by r, we have

$$p_A = r p_B^n.$$

Now the concentrations of the two gases are proportional to the partial pressures p_B and p_A, $p_A = ha$ and $p_B = hb$, where h is the proportionality factor. Accordingly, putting $rh^{n-1} = k$, we have

$$a = kb^n.$$

The Temperature Effect.—It can at once be said, from the general principle of equilibrium, that a rise of temperature will bring about that process which is opposed to the rise of temperature, *i.e.* the equilibrium will be displaced in such a direction that the reaction is accompanied by absorption of heat. In the case of nitrogen peroxide this is the decomposition into the simpler compound, so this will increase with rise of temperature. This conclusion is borne out by experiment.

This is very clearly demonstrated if nitrogen peroxide vapour is enclosed in a sealed tube. While at the ordinary temperature the contents of the tube are only slightly coloured, the colour becomes rapidly darker on heating the tube, and the original colour is regained on cooling. A similar tube which is not warmed serves for a comparison.

An equation for the effect of temperature on equilibrium can be obtained in a way similar to that which led to the vapour pressure formula on p. 78. It is based on the principle that the ratio of the heat transformed into work to the total amount of heat set in motion by a reversible cycle working between two temperatures, is the same as the ratio of the difference of temperature to the absolute temperature, or

$$d \lg r/dT = L/RT^2.$$

The work absorbed when, in a large amount of gas, one mol of a gas is changed into n mols of another, is $RT(\lg p_A - \lg p'_A) - nRT(\lg p_B - \lg p'_B)$, since one mol disappears and n mols result; the new partial pressures are distinguished by a dash. The change in this work will be expressed by $RT\,d \lg(p_A/p_B^n)$, and the equation representing this change with temperature, or the work gained in a cycle between the temperature T and T + dT, becomes

$$RT\,d \lg(p_A/p_B^n)/L = dT/T,$$

in which L is the amount of heat absorbed during the transformation of one mol of the gas. Now the ratio p_A/p_B^n is the equilibrium constant r (see above); the equation thus simplifies to

$$d \lg r/dT = L/RT^2.$$

This equation (van't Hoff, 1885) agrees in form with that deduced for the change of vapour pressure with temperature (p. 79), except that on the left side we have the quotient of the partial pressures (or powers of them) instead of the pressure. It will be seen later that this formula holds for all kinds of equilibrium, the logarithmic term always being the equilibrium coefficient referred to the given pressure.

If the variation of r, *i.e.* of the equilibrium state with temperature is known, the heat of reaction L can be calculated from the equation, and *vice versa*. It has been confirmed in many instances of widely different nature, and has proved of use in calculating heats of reaction which could not be determined directly. Thus, the heat absorbed by the decomposition of iodine, $I_2 = 2I$, at very high temperatures (p. 167) has been calculated to be 119 kj. (Boltzmann, 1884).

Equilibrium in Liquids.—States of equilibrium similar to those in a mixture of mutually convertible gases can occur in liquids which can be changed into each other. Liquid nitrogen peroxide is undoubtedly a mixture of the two forms, although N_2O_4 predominates, and the ratio of the two is altered with rise of temperature in favour of the simple form. But only the general part of the laws developed for equilibrium in gases remains in force, that part relating to the direction of the displacement produced by altered conditions:

increase of pressure will always promote the reaction which is accompanied by diminution of volume, and rise of temperature the reaction which absorbs heat. The quantitative laws, deduced from a calculation of the work by means of the gas laws, do not apply where the gas laws lose their validity. The gas laws hold for dilute solutions, if osmotic pressure is substituted for gas pressure (p. 173); but it is at present impossible to calculate the work in a general manner for concentrated solutions, and the equations therefore are no longer applicable.

Heterogeneous Equilibrium.—Further instances of equilibrium of the first order arise when several phases are present. The essential features of such equilibria have been described in the chapters on change of state (pp. 55 and 99); it only need be added that the relations there developed are equally true, whether transformations undergone by the substances are isomeric or otherwise. The only difference is that equilibrium is usually more slowly attained in chemical transformations.

For instance, liquid nitrogen peroxide has a definite vapour pressure at each temperature, although neither as a liquid nor as vapour is it a single substance in a chemical sense. Similarly the equilibrium between solid cyanuric acid, $H_3C_3N_3O_3$, and the vapour of cyanic acid, HCNO, which is formed when cyanuric acid is heated, depends on the temperature only, although a chemical change takes place on vaporisation. The same holds for gaseous cyanogen and solid paracyanogen, which is a polymer of the former.

The same considerations apply to the equilibrium between solid and liquid. A solid and its fused liquid follow all the laws developed on p. 99 for the case of simple fusion, no matter how the two phases may differ chemically, provided that they are and remain of the same composition. The phases do not even need to be single substances; we shall find in the "cryohydrates" systems which in the solid state may be mixtures of any number of components, and yet obey the melting-point laws, because they fulfil the conditions that the solid and the liquid phases have the same total composition and are mutually convertible. These considerations allow us to bring all the possible cases of equilibrium of the first order under the laws which have been discovered.

Phases and States of Matter.—In conclusion an important point remains to be touched upon. There cannot be more than one gas phase in a system, as all gases dissolve each other in all proportions. The number of liquid phases cannot exceed, so far as present experience goes, the number of components present; no equilibria of the first order are known with more than one liquid phase.[1] Liquids and gases may be pure substances or solutions. Any number of solids may participate in an equilibrium; in most instances they

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[1] Liquid crystals are not to be regarded as liquids in the above sense.

are pure substances. Solid solutions are possible and are known, but they seldom occur, and they will be left out of consideration at present.

Supersaturation.—In all equilibria between several phases, a new phase, which is not yet present, does not necessarily make its appearance when it can coexist with the other phases under the given conditions. On the contrary, supersaturation must be regarded as a general peculiarity of heterogeneous systems, and it appears justifiable, on the ground of present experience, to extend the terms stable, metastable and labile to all such cases, and not to restrict them to the equilibrium between a liquid and its vapour. The ease with which supersaturation can be produced differs enormously, as also does the extent of the metastable region.

If the metastable region has been exceeded, and a new phase appears spontaneously, it is remarkable that the phase which appears is not the most stable phase under the conditions, but is the least stable, *i.e.* the next in stability to the phase which is undergoing transformation. This phenomenon is extraordinarily extensive. For example, sulphur always separates from its vapour in the form of drops of liquid, even when the temperature is far below the melting-point. Mercuric iodide always precipitates from vapour as the unstable yellow form, although the transition temperature is about 140°. This phenomenon is quite general in character, and is not limited to equilibrium of the first order, but holds in all changes of state, and especially in chemical reactions in the strict sense.

CHAPTER XIII

CHEMICAL EQUILIBRIUM OF THE SECOND ORDER

General.—From the definition of equilibrium of the first order (p. 305) we infer that in an equilibrium of the second order the composition of all the phases can be represented as the sum of two components, which may be either chemically simple or compound substances. Consequently the order of a given system will depend on the kind of transformations and on the external conditions which are taken into consideration. At temperatures not exceeding a few hundred degrees, for example, the possible transformations of water are of the first order; but if we pass to temperatures at which the decomposition of water into oxygen and hydrogen is perceptible, the equilibrium is of the second order, because the phases now resulting can only be expressed by independent amounts of the components oxygen and hydrogen. It is a matter of choice which substances are selected as components; not so the number of components. Thus there is at high temperatures equilibrium between calcium oxide, carbon dioxide and calcium carbonate, and each of the phases can be represented by means of two (or one) of these substances; there are therefore two components. Any two of the three may be chosen; but if $CaCO_3$ is one, negative amounts will have to be used. This is avoided by taking the other two substances as components.

It must be remembered at the same time that all the components are not necessarily present in analytically recognisable quantity in every phase, although it is convenient to make such an assumption theoretically. As in all probability there is no substance absolutely non-volatile or absolutely insoluble, it may be assumed that all the components are present in all the phases, but some of them only in an immeasurably small amount.

Solutions.—One of the most important groups in equilibria of the second order comprises the two component systems which form a phase of continuous variable composition. Such phases of two or more components are called solutions; we shall proceed to consider their properties more closely. The relations discussed on

p. 170 *et seq.* form only a small, though important part of the theory of solutions, and were there dealt with for special reasons.

If a solution is considered by itself, it differs in no way from a pure substance, since it has, like it, a fixed density, refractive index, etc., and also a definite chemical composition. The essential difference between pure substances and solutions appears only when they are subjected to transformation, or when several substances of similar nature are compared. During transformation into other phases the properties of pure substances do not change, while, on the contrary, the properties of solutions do vary. Pure substances can be changed into other pure substances without residue, while solutions yield other solutions or mixtures. Connected with this is the fact that the analytical composition of pure substances changes step by step, in accordance with the law of combining weights, while the composition of solutions can be changed little by little between certain limits, the properties of different solutions being more nearly alike, the smaller the difference in their composition.

To find out, for instance, whether a liquid is a pure substance or a solution, we alter the temperature so that it either freezes or boils. We follow the process with the thermometer: if the temperature remains constant from the first appearance of the solid phase to the disappearance of the last drop of liquid, we infer that it is a pure substance; if not, that it is a solution. The second inference is conclusive; the first not quite so, as there are certain exceptional solutions (see below) which freeze at constant temperature. Further, we may heat the liquid until it boils and follow the thermometer from the beginning until the last drop has distilled over. Again a change of temperature proves that it is a solution, while constancy of temperature indicates that it is probably a pure substance, but does not prove it with certainty. But if a liquid both freezes and boils at constant temperatures, we may conclude that it is a pure substance.

By separating the first or last fractions with different properties produced in these processes, and by repeating this treatment, every solution can finally be decomposed into a definite number of pure substances. On bringing them together again the solution is once more obtained with all its former properties. Solutions must be regarded as products of the appropriate pure substances, which are called its components; formation and decomposition of a solution is a reversible process, so far as the components are concerned. On this account it is not usually considered a direct scientific problem to investigate the properties of a solution obtained in some reaction; it is first subjected to the fractional formation of new phases or products of transformation, until the solution is separated into the pure substances composing it. Chemical preparations and syntheses consist largely and essentially in separating pure substances from the solutions obtained as the result of the reactions. And, as proof that this has been accomplished, the products must be shown to have constant boiling- or melting-points. Until this has been attained, the operation of fractional separation of the phases, such as fractional distillation and fractional crystallisation (from the fused mass or from solution) must be repeated, as the substance is not pure, but a solution or a mixture.

Gas Solutions.—Gases form solutions with each other under all conditions, since all gases are miscible in all proportions (provided they do not chemically react with each other). The properties of the product are the sum of the properties of the components; in other words, they are additive. This important law, first stated generally by Dalton, provides an answer to all the questions which now arise.

It can be put in the following very intelligible form: each single gas in a gaseous solution behaves in every respect as if it alone were present.

One of the commonest applications of the law is to pressure. All the reactions in a gas mixture which depend upon the pressure of a gas take place as if each component exerted the pressure, which it would do if it alone occupied the space. This pressure is called the partial pressure of the component, and it alone counts in the problems before us (*i.e.* chemical equilibrium).

The law assumes the gases to be uniformly distributed through the mixture. This takes place spontaneously by diffusion, if the components are left long enough in contact; it is, accordingly, the only state which comes into the question of equilibrium. Just as a gas can only be at rest in a space when the pressure is the same throughout, so a gas solution is not at rest until all the partial pressures are the same throughout.

The validity of this law of Dalton is as wide as that of the gas laws; irregularities begin when the density is so great that the gas laws cease to represent the actual facts.

Gas solutions behave like pure gases with respect to temperature and pressure, as they follow the laws of Boyle and Gay-Lussac. To ascertain whether a gas is pure or a solution, it must be converted by cold and pressure into the liquid or solid state, observations being made whether complete transformation takes place under constant or varying conditions (of pressure or temperature). If this cannot be done, any other conversion into a liquid or solid phase (by solution or absorption, or even by chemical action) can be used. Separation can also be effected by driving the gas through porous septa (porous earthenware, graphite plates), as components of smaller density pass through them from solution more rapidly, and therefore accumulate in the first fractions, while no separation occurs with pure gases.

There is little to be said about solutions of liquids and solids in gases. If a volatile liquid is placed in a gas, it evaporates just as in a vacuum, for, according to Dalton's law, its vapour pressure is the same, whether a gas is present or not. The law is valid within the same limits as Dalton's law, and irregularities appear at higher pressures.

Another reason for irregularities is that the gas dissolves in the liquid, and lowers its vapour pressure according to the general rule (p. 178). This effect is noticeable only when the gas is readily soluble, and disappears in many cases.

The same is true for solutions of solids in gases. They can only occur with volatile solids. Their vapour pressures in gases are the same as in a vacuum. Since gases do not dissolve to a marked extent in solids, they are simpler than solutions of liquids, for this cause of irregularities is absent. At very great pressures solids dissolve in gases to a greater extent than in a vacuum, partly because gases then act like liquid solvents, and also because the vapour pressure of a solid (and of a liquid) is directly increased by pressure. The latter effect is easily understood, if we recollect that pressure increases the density of the substance, which then requires a denser vapour for equilibrium.

Solutions of Gases in Liquids.—The behaviour of liquid solutions is much more varied. The laws of dissolved substances in dilute solutions have been already dealt with (p. 170); we have now to consider the equilibrium relations occurring in the formation of solutions.

Gases, liquids and solids can form liquid solutions with liquids, and the laws governing these three classes must be discussed separately.

The equilibrium between gases and liquids is governed by Henry's law (1803), which states that the amount of gas dissolved by a liquid is proportional to the pressure, and varies with temperature. Dalton (1805) extended the law to the components of gas solutions, the partial pressures alone being taken into account.

As the volume of a gas is inversely proportional to its pressure, Henry's law can be stated as follows: the volume of a gas absorbed by a quantity of liquid is independent of the pressure.

If the quantity of gas in unit volume (of the gas space as well as of the solution) is called the concentration, the law can also be expressed in this way, that under given conditions the ratio of the concentration in the gas to that in the liquid is constant, independently of the pressure. This ratio is the solubility coefficient, or shorter, the solubility of the gas.

Bunsen's absorption coefficient (1885) is closely related to this value. It is the volume of gas, reduced to 0° and 760 mm.

pressure, which is absorbed by 1 ccm. of the liquid at the same pressure; the difference between it and the solubility as defined above is that the volume is reduced to 0°, *i.e.* is divided by $1 + {\cdot}00367\,t$. It seems more convenient to give the volume of gas for the temperature at which the solubility has been determined, but Bunsen's definition is still largely used, and must be mentioned.

The calculation of an absorption experiment, in which the volume of liquid v has dissolved a volume of gas V at the temperature t and pressure p, by Bunsen's method is as follows:—the gas volume is reduced to normal condition by multiplication with $p/76(1 + \alpha t)$, then by multiplication with $76/p$ the amount of gas is calculated which would dissolve at normal pressure according to Henry's law, then finally division by the volume of liquid v gives the amount of gas for unit volume of liquid. The absorption coefficient is thus:

$$\beta = \frac{V}{v} \cdot \frac{p}{76(1 + \alpha t)} \cdot \frac{76}{p} = \frac{V}{v(1 + \alpha t)}.$$

The solubility, as defined above, is simply $\lambda = \frac{V}{v}$.

Bunsen and his pupils have determined the absorption coefficients for a large number of gases in water and alcohol at temperatures between 0° and 20°. The numbers are not large as a rule, varying for the "permanent" gases—nitrogen, hydrogen, oxygen, carbon monoxide, methane—between 0·02 and 0·05. The easily condensed gases, such as carbon dioxide, nitrous oxide, sulphur dioxide, have coefficients varying between 1 and 4. These numbers are for water; they are from two to eight times as large for alcohol, but the two series are not proportional.

In most instances the solubility diminishes with rise of temperature. This is connected with the positive heat of solution of gases in most liquids.

These laws are valid to the same extent as the gas laws: they are limiting formulæ, which approximate more or less to the actual facts, and usually more so when the solubility is small and the pressure low. Still, Henry's law holds to within one per cent up to 4 atmospheres in the case of so soluble a gas as carbon dioxide, while all gases show irregularities at 10 atmospheres.

Gases the solubility of which is very large, amounting to several hundred times the volume of the liquid, do not obey Henry's law. In such cases there are reasons for the belief that chemical action takes place between the gas and the liquid, so that part of the dissolved gas is chemically changed, and only the unchanged part (the amount of which is usually unknown) counts in the final equilibrium. In these cases the quantity of gas absorbed increases less rapidly than does the pressure. Sometimes the irregularities which occur at low temperatures disappear at higher temperatures, where the solubility is less. Thus, sulphur dioxide obeys Henry's law above 40°, but not below it; ammonia in water does not obey the law below 100°.

The solubility is usually diminished when gases are absorbed in solutions of various substances instead of in pure water. Dissolved gases are evolved when solids are dissolved in the liquid. In some cases, as in those investigated by Raoult (1874), in which sodium hydroxide and potassium hydroxide solutions were saturated with ammonia, it was found that the decrease is proportional to the amount of solid. Setschenoff (1875) obtained similar results for carbon dioxide and various salt solutions, but, in addition to the solution effect, there were chemical reactions between the carbon dioxide and the dissolved salts in certain cases, and these complicated the phenomena. In the simplest cases the dissolved quantity was made up of one part independent of the pressure and proportional to the amount of salt (the chemically combined part), and of another part in simple solution and proportional to the pressure. But in other cases the first part was also dependent on the pressure, though to a less extent than Henry's law demands; there was chemical action in these cases, but it was incomplete and varied with the pressure.

Supersaturation.—Supersaturation occurs very readily in solutions of gases in liquids, probably more easily than in any other case. A solution, when brought under a lower pressure than the saturation pressure, does not give off the gas, but remains homogeneous. The supersaturation must be really considerable before it spontaneously ceases.

If a gas solution is saturated at a given pressure, and the pressure is then lowered, the corresponding amount of gas does not instantly leave the solution. Extensive contact between the solution and the gas at the reduced pressure, or better still, another gas in which the partial pressure of the dissolved gas is zero, is necessary to remove the supersaturation. For this reason the addition of porous powders, which enclose large quantities of air, or violent shaking, which spreads numerous bubbles of gas through the liquid, or, finally, boiling the solvent, when the bubbles of vapour have the same effect, are particularly effective in this respect. Supersaturation persists for a very long time in carefully cleaned (with sulphuric acid, alkali, etc.) glass vessels.

On the other hand, each bubble of gas, whether the same or some other gas, acts as a nucleus (p. 68) which assists the formation of the new phase. This action is local in its effect; when the bubble has risen to the surface, the liquid still remains supersaturated, and spontaneously evolves no more bubbles, unless, indeed, a portion of the bubble has remained behind.

In this automatic removal of nuclei is to be found the real cause of the stability of supersaturated gas solutions. When a solid separates out from overcooled liquid it remains in it, and the crystallisation does not cease until the supersaturation is removed; but a supersaturated gas solution expels nuclei which may be present and remains supersaturated.

These phenomena can be conveniently observed with the ærated waters (soda water, etc.) used as beverages, which are charged with carbon dioxide at a pressure of about 4 atmospheres. When the first effervescence on pouring it into a glass is over, small bubbles are usually formed at places where the glass has been scratched, and some air has been imprisoned, and rise in a fine stream. If the glass has been carefully wetted beforehand, the liquid remains quiet. Any object to whose surface gas adheres, therefore especially porous substances, restarts the evolution of gas. If a clean capillary, closed above and enclosing air, is dropped into the liquid, the bubbles are seen to rise from the interface of the air and the liquid, showing that the gas is only set free there.

Consideration of surface-energy (p. 80) shows that supersaturation must take place if gas nuclei are absent. Since the surface tension of a liquid tends to diminish the surface, there must be a greater pressure in the interior of a spherical bubble than at a plane surface under the same circumstances, and the theory of capillarity gives for this the equation $p = 2\gamma/r$, where p is the pressure, γ the surface tension and r the radius of the sphere. If, therefore, a bubble of gas is formed spontaneously, it will be under a far greater pressure than corresponds to saturation under the given conditions.

It appears from this that a bubble could not be formed spontaneously at all. For, as at the first instant the bubble must be infinitely small, the pressure, according to the equation, must be infinitely great. The spontaneous formation of bubbles shows that the assumption that the properties of a liquid remain the same up to infinitely small dimensions, is incorrect. The same conclusion has been reached from other considerations (p. 83). If the limit for the ordinary properties of liquids is put at 10^{-8} cm., the pressure in a bubble of this radius in water at room temperature is calculated to be 15,000 atmospheres. Apparently nothing like this degree of supersaturation is necessary to cause spontaneous evolution of gas.

These considerations are applicable to supersaturation of solids or liquids, as a substance must be more soluble, owing to surface energy, the more finely divided it is. This might be inferred from the analogy of the increased vapour pressure of small drops (p. 84); it might also be reached from the consideration that the work on dissolving another phase is smaller the more energy has been taken out by the formation of a common surface with the solvent.

Equilibrium between Phases.—The general statement which follows applies to all heterogeneous systems. All phases which are in equilibrium with each other, can replace each other in any other equilibrium system, in which one common component of this phase is concerned. This is a property of the intensity factor of chemical energy (p. 246), the chemical potential. Just as two objects which have the same temperature or electrical potential as a third object are equivalent in these respects, so there is equality of chemical potential between two or more phases in equilibrium, by means of which a condition is reached chemically, similar to that which equality of temperature produces as regards heat.

To make this important general law clearer, let us think of a solution of hydrogen in water, in equilibrium with hydrogen gas at atmospheric pressure. A piece of palladium is placed in the solution, and it takes as much hydrogen from the solution (if its concentration is kept constant) as from the gas, although the concentration in the aqueous solution is 50 times smaller than in the gas, and 50,000 times smaller than in the metal.

This rule is a special case of the second law of energetics, and the proof is that a perpetuum mobile of the second kind could be constructed if it were not true. Let us suppose that palladium takes up less from the solution than from the gas. The metal is first saturated in contact with the gas, and is then placed in the solution. As it contains more hydrogen than when saturated in contact with the solution, hydrogen will leave the metal for the solution, which will become supersaturated with the gas. This excess of gas will raise the pressure of the gas in contact with the solution, and work can be obtained when the gas is expanded to atmospheric pressure. The palladium can now be again saturated with this gas, and the process repeated, an unlimited amount of work being thus obtainable by a cycle at constant temperature. This is a contradiction of the second law, and therefore is impossible. A similar reasoning applies if the contrary assumption regarding saturation is made.

The law of the interchangeability of phases which are in equilibrium applies only to the components common to them all. If two phases, consisting of the components A, B, C and A, D, E, are in equilibrium, and the former is brought into equilibrium with a third phase A, E, F, then A, D, E and A, E, F are in equilibrium with respect to A, but are not necessarily so with respect to E. Attention must be paid to this in applying the law of equality of chemical potential. The peculiarity is that there are as many different kinds of chemical potential as there are components present, whereas, *e.g.* there is only one kind of temperature.

Solutions of Liquids in Liquids.—Liquid solutions are by no means so simple as solutions of gases. For one thing there is not the universal solubility as with gases: many liquids only partially dissolve each other. Then the additive law does not hold for liquid solutions. It is rather a limiting case which is very seldom reached, while greater or smaller deviations form the rule.

These divergences have frequently been studied, without any general conclusions having been reached. The volume of a mixture of two liquids never is the sum of the partial volumes, but usually there is contraction, although occasionally there is expansion. Owing to this, it is impossible to calculate by simple proportion the content of a solution from its density; for every pair of liquids (and, strictly, for every temperature) the connexion between density and composition has to be empirically ascertained.

The contraction on mixing two liquids is well shown when a tube, one metre in length, is half filled with water, and is filled up with a layer of alcohol. When the two are thoroughly mixed by shaking up the closed tube, an empty space, several centimetres in length, appears in spite of the higher temperature.

Divergences from the additive law are especially great when water forms one component, and are least with mixtures of saturated hydrocarbons, or their halogen derivatives, of esters, etc. Apparently liquids which are shown by the surface-tension method (p. 168) to be more polymerised than the vapour have the greatest effect upon each other in solution, and it seems justified to attribute these divergences from the additive law to the mutual changes in the molar weight of the liquids.

Vapour Pressure of Solutions.—The most definite information concerning the condition of liquids in a solution is got from the vapour pressure, or the concentration of the vapour. This is a measure of the active mass of the liquid, *i.e.* of the amount which participates in any equilibrium.

The proof of this consists in the general law of the interchangeability of phases (p. 319), along with the fact that the simple law of mass-action holds for gases and vapours.

The vapour pressure of a liquid in its solutions follows simple laws, if it forms either a very large or a very small fraction of the solution. In the former case we know (p. 179) that any substance diminishes the vapour pressure of its solvent by an amount represented by the ratio $N_2/(N_1+N_2)$. Here N_1 is the number of mols of the solvent (substance present in large amount), and N_2 the mols of the solute[1] (or substance present in smaller amount). For the sake of brevity we may call $N_1/(N_1+N_2)$ the molar fraction of N_1, and $N_2/(N_1+N_2)$ the molar fraction of N_2.

If the one molar fraction is plotted from left to right on a horizontal straight line, and the corresponding vapour pressures on

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[1] The terms solvent and solute must not be taken to mean that there is any real difference in behaviour of the two substances composing the solution. No such difference exists, and the words merely express the relative amounts as stated in the text.

the vertical line, the end of the curve to the right will be a straight line directed to the axis, Fig. 36. In this region the vapour pressure is equal to the vapour pressure of the pure substance, multiplied by the molar fraction.

To the left, where the liquid contains only small amounts of the substance, the ratio between partial pressure and molar fraction is given by Henry's law. Obviously it does not matter at what pressure the gas is dissolved by a liquid; if a substance can form a gas or vapour phase at all, its concentration in the solution will be in a constant ratio to that in the vapour, so long as the solution is not too concentrated. In this region the vapour pressure curve will also be a straight line, which passes through the origin, because for zero amount of solute the vapour pressure will also be zero, but its direction is not necessarily the same as that of the latter part of the curve. Rather, the beginning of the curve runs flatter or steeper as the solubility of the vapour in the other liquid is large or small.

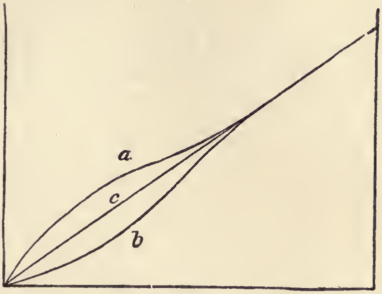


FIG. 36.

If we assume that the middle part of the curve takes the simplest course, the vapour pressure curve of the one component of the liquid solution has the form of a, b, or c in Fig. 36. The first form a occurs when the solubility is very small; the form b corresponds to a large solubility. The simplest case is represented by c, when the partial pressure is equal to the vapour pressure of the pure liquid, multiplied by the molar fraction; the two ends of the curve follow the same law, and usually also all through the middle portion.

The same considerations apply to the second component; its vapour pressure curve can be any one of the three forms. Theory shows that both components of a given pair of liquids must have partial pressure curves of the same form; they both belong to the same type, whether a, b, or c.

The results of the few investigations on this subject have shown that liquids which are very similar and are not polymerised usually dissolve in each other in all proportions, and conform fairly closely to type c. Form b occurs with liquids between which there is strong chemical action, while a is found in pairs, which are almost on the point of separating (see below). The two partial pressure curves of the vapours of a mixture run contrary to each other, and their sum gives the curve of the total vapour pressure, which lies between the values of the two components. The form of this curve varies according to the form of the partial pressure curves. The simpler types are shown in Fig. 37.

If they are straight lines, the sum is the same, and we have type 1. The rule can be reversed; if the total pressure curve is a straight line, so are the partial pressure curves.

Curves of the form a in Fig. 36 give rise to total pressure curves of the type 2 and 3 in Fig. 37. Such convex curves may either rise steadily as No. 2, or pass through a maximum as No. 3. The same difference is shown in types 4 and 5, which result from the form b.

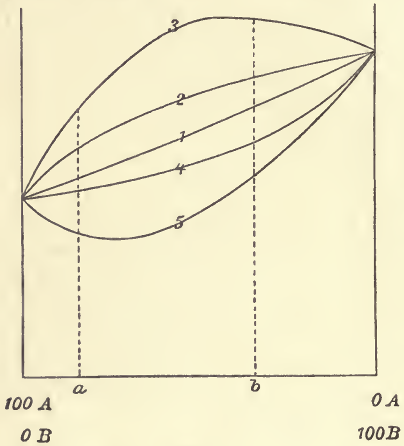


FIG. 37.

Distillation of Solutions.—These total pressure curves are of importance, because they indicate the behaviour of substances on distillation or evaporation.

The composition of the vapour is usually different from that of the liquid. The direction of the variation is given by the total pressure curve, the rule being that the composition of the vapour lies in the direction of the ascending side. Suppose the molar fraction of the liquid to be represented by a in Fig. 37, then solutions, the curves of which are represented by 1, 2, 3, 4, evolve vapours the composition of which is represented by a point lying to the right of a, while the vapour of 5 is given by a point to the left of a. A liquid of the composition represented by b gives, in the case of 1, 2, 4 and 5, vapours, the composition of which lies to the right of b, while for 3 it lies to the left.

Owing to the evolution of such vapours the liquid changes its composition in the contrary direction, so the general rule is: during distillation the liquid changes its composition in the direction of the descending part of the vapour pressure curve, the distillate changes in the direction of the ascending part.

The cause of this is found in the circumstance that these states are equilibria. This necessitates that the evaporation at constant temperature should change the solution so as to lower the vapour pressure, otherwise the change once started would continue spontaneously.

Singular Solutions.—Curves 3 and 5 represent a special case, there being a maximum and a minimum. According to the above rule the vapour at these points cannot differ from the liquid in either direction, and must have the same composition as it. The residue, too, is not changed by distillation, and such a solution must distil at constant temperature, *i.e.* like a single substance.

These singular solutions of constant boiling-point have frequently been observed, and were formerly taken for chemical compounds: this error survives even to this day. That they are solutions is shown by the fact that their composition does not usually follow any simple stoichiometric ratio. Further, vapour density determinations show the absence of chemical combination, and, finally, the composition of the constant boiling-point solutions varies continuously with pressure.

It follows from this that solutions of two volatile components can be separated into their components by distillation only if their vapour pressure, plotted against composition at constant temperature (or what is practically almost the same, their boiling-point at constant pressure), shows no maximum or minimum. If these occur, the separation by distillation proceeds as far as the separation of the singular solution from the component present in excess.

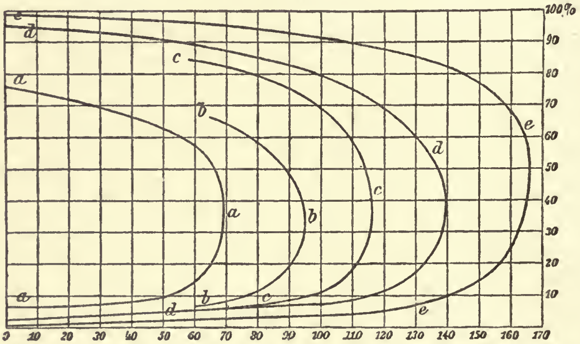
Limited Solubility.—In many cases the mutual solubility of two liquids is limited. If small quantities of a liquid B are added to a liquid A, they dissolve at first: but when a definite concentration has been reached, which depends on the temperature (and, to some extent, on the pressure), no more B goes into solution, but remains beside the "saturated" solution of B in A. The second liquid consists mainly of B, but always contains some A. Further addition of B increases the quantity of the second layer without altering its composition. In other words, there are two saturated solutions: one mainly A with some B, the other mainly B with some A. This phenomenon is general; a liquid A never shows limited solubility for B without B also taking up some A to form a saturated solution.

From the phase rule point of view, the case is characterised by the presence of three phases in a two component system, the phases being the two layers of liquid and the vapour. There remains one degree of freedom, and if the temperature is fixed, thus disposing of one degree of freedom, a change in the relative amounts can have no effect on the equilibrium. A change in the quantity of the two components will change the quantities of the phases, but not their composition; as that has no effect on equilibrium, the conditions of the phase rule are satisfied.

Critical Solution Point.—The effect of temperature on partially miscible liquids is usually to increase the mutual solubility. If the temperature is measured horizontally and the composition (expressed as molar fractions or as parts by weight) vertically, there are two values for each temperature, one for each layer. With increase of temperature these points generally lie closer together, *i.e.* the two layers become more alike, and finally become identical. They then no longer remain separate, but mix to a uniform whole. Fig. 38 shows this for some aqueous solutions.

This transition is so similar to the critical point in the transition of liquid to vapour (p. 63) that it is called the critical solution point. In general, a critical point is one where two phases, after continuous approximation to each other, become identical and merge into one.

The critical solution point is usually reached at higher temperatures, but cases are known where the solubility increases with falling temperature, leading to a "lower" critical point. Examples of the former are isobutyric acid and water, phenol and water; of the latter, triethylamine and water.



a Phenol; *b* Salicylic acid; *c* Benzoic acid; *d* Aniline phenolate; *e* Aniline.

FIG. 38.

The composition at which the two solutions are close to the critical point is the critical concentration, corresponding to the critical density in the simple case. But there is no critical pressure, for the critical solution temperature is itself a function of the pressure, if the system consists of the two liquid phases without vapour. Still, the effect of pressure is so slight that there is difficulty in proving it at all.

Vapour Pressure and Limited Solubility.—The vapour pressure of such solutions shows the usual variation with composition, until saturation is reached. When the solution has separated into two layers, further addition of the one component does not alter the composition, and only the relative amounts vary. Accordingly, the vapour pressure cannot alter so long as the two layers remain, for ti depends only on the composition of the liquids, not on their amount. Further, we may conclude that the vapour pressure of each layer is the same and not only the total pressure, but also the partial pressures (Konowaloff, 1881).

The proof of this is again found in the rule that what is in equilibrium in one way must be in all. If the two solutions are in equilibrium when in direct contact, a perpetuum mobile of the second kind would be possible if their vapours were not in equilibrium too, therefore the vapours singly and together must have the same pressure.

The total vapour pressure curves for partially miscible liquids are shown in Fig. 39; the differences depend on whether the total pressure in the heterogeneous middle portion lies between the pressures of the pure components, the curve s, or above them, r. It cannot be below them. The behaviour on distillation is seen at once from the curve, as on p. 322; in particular, the distillate has a constant composition independently of the relative amounts of the two layers, so long as two layers remain in the retort.

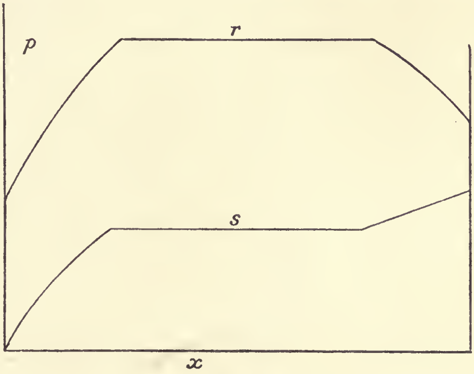


FIG. 39.

Insolubility.—The mutual solubility of liquids may be so slight as to elude observation; such substances are said to be insoluble in each other. There is every reason to believe that, strictly speaking, insolubility does not exist, the differences being quantitative. Apart from the fact that the limit between soluble and insoluble liquids is continually being displaced, owing to the improvements in analytical methods, there are theoretical grounds against the assumption of absolute insolubility.

The smaller the mutual solubility, the smaller is the diminution of vapour pressure, and the vapour pressure of a mixture of the two liquids approaches the sum of the vapour pressures of the components. The boiling-point of such mixtures is far lower than that of the components, as boiling commences when the sum of the two vapour pressures is the same as the external pressure.

On distillation the two immiscible liquids go over in constant proportions, independently of the relative amounts in the retort, since the vapour consists of the vapours of the components in the ratio of their vapour pressures. Since the two amounts are as the products of the vapour pressure and the density, or of vapour pressure and molar weight, the molar weight can be found if the vapour pressure is known.

Generally the vapour pressure is unknown too. It can be found from the boiling-point of the mixture, if the relation between vapour pressure and temperature is known for the other liquid. This is, of course, below the boiling-point of the more volatile component, and is the temperature at which the sum of the partial pressures of both vapours is equal to atmospheric pressure. The partial pressure of the second liquid at the temperature of their common boiling-point is then subtracted from the atmospheric pressure, and the remainder is the partial pressure of the other substance at the same temperature. The method is not very accurate.

Supersaturation phenomena have not been observed with certainty in solutions of liquids in liquids.

Solutions of Solids in Liquids.—Unlimited solubility, which always occurs with gases, and is of frequent occurrence with liquids, is excluded with solids in liquids; solubility is limited, and there is a state of saturation. When a solid is added to a liquid, at first it dissolves; at a definite concentration, which depends very markedly on the temperature but only to a slight extent on the pressure, saturation occurs, *i.e.* further additions of solid lie undissolved in the liquid. According to the general laws of phase equilibrium, the saturation concentration is absolutely independent of the quantity of solution and of solid.

There are many combinations of liquids and solids which we are accustomed to call insoluble. What has just been said (p. 325) about insolubility applies here, and it is better to suppose a certain degree of solubility, however small, in every instance. It is just in solutions of solids that electrical methods have in recent years enabled investigators to demonstrate the presence of solubility, and to measure its amount in the case of substances (such as silver bromide and silver iodide) which were previously assumed to be absolutely insoluble.

Solubility determinations are made by bringing the solid and the solvent together and allowing them to interact at constant temperature. The velocity of saturation varies very much with the nature of the substances; it is therefore of advantage to increase the velocity as much as possible by finely pulverising the solid, and by constant stirring of the mixture.[1] Either the temperature is ascertained at which the (previously weighed) components just dissolve, or excess of solid is employed, and the clear solution analysed after saturation at constant temperature. The latter

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[1] If the solid is present in very fine powder, its solubility is increased owing to the surface energy effect, just as the vapour pressure of very small drops is increased. Too fine division must be avoided, or the mixture must be left to itself for a long time, when the smallest particles will be "eaten up" by the larger, *i.e.* they will dissolve, while the larger ones grow. This process can easily be observed under the microscope.

method is usually the more accurate, but the former is more generally applicable, and, as it can be carried out in sealed tubes, can be used with liquids which cannot be exposed to the air, or whose boiling-point lies near or below the working temperature. On the other hand, it presupposes a sufficiently high rate of saturation.

Another form of the second method is to prepare first of all a supersaturated solution (see below), and keep this in contact with excess of solid at constant temperature, until equilibrium is established. Simultaneous application of this and of the ordinary method affords the greatest security against errors of saturation.

The state of saturation in the equilibrium between a solid and its solution is conditioned by the nature of the solid, and changes with it. Thus each allotropic form of a substance has its own particular solubility, just as its different states of aggregation have, and the values are equal only at points where the different forms can exist in presence of each other and of the solution. The same holds for the various solid compounds of the solid component with the solvent, *e.g.* the different crystalline hydrates of salts. Solubility data are indefinite unless the form of the solid is given, to which the numbers refer.

Supersaturated Solutions.—If no solid is present, the concentration of the solution is not fixed. This is true whether the concentration is below or above the saturation value. Solutions which contain more of a solid than corresponds to saturation are called supersaturated. This state depends on the form of the solid, just as saturation does, and a solution can be supersaturated with respect to one form, and unsaturated with respect to another. If a small quantity of the solid is placed in a supersaturated solution, the solid increases in amount until the concentration has fallen to saturation point.

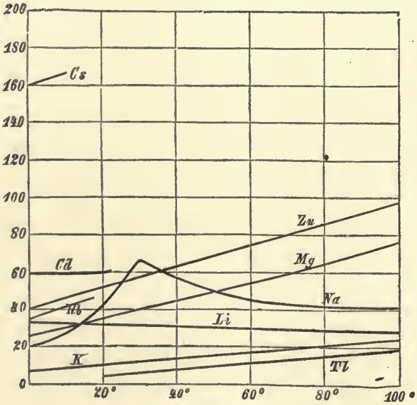
The quantity of solid which will bring about crystallisation is very small, but not infinitely small. The limit is about the same as that which was found to start the solidification of overcooled liquids, and is about 10^{-8} to 10^{-10} g. As the solubility increases when the particles are very small, particles of about these dimensions only act on strongly supersaturated solutions, and the supersaturation must be greater the smaller the particles are.

Supersaturated solutions can be obtained by any method which permits of the accumulation in the solution of a greater amount of the solute than is sufficient for saturation. The simplest way is with substances which are more soluble at high temperatures, when a solution saturated at a higher temperature is carefully separated from every trace of the solid, and is then cooled. But any other method, as *e.g.* production of the substance within the solution by chemical means, can be employed, which yields the necessary excess.

Supersaturation has been most fully studied in the case of sodium sulphate. When crystallised sodium sulphate, Na_2SO_4, $10H_2O$, is added to half its weight of water, and heated to boiling in a flask closed with a plug of cotton wool, the solution when cooled is supersaturated with respect to Glauber's salt (the deca-hydrate), and crystallises at once on addition of a small particle of it. As ordinary dust always contains some of it, crystallisation takes place in a short time, if the flask is merely left open.

If the closed flask is cooled to – 10°, a salt with $7H_2O$ separates, as the solution first becomes supersaturated with respect to it. The supernatant liquid is saturated with the new solid, for the salt dissolves on heating and crystallises out again on cooling. But this solution remains supersaturated for the decahydrate, and forms this salt, whenever a "nucleus" of it gets into the liquid.

Substances differ greatly in the ease with which they form supersaturated solutions; with some the degree of supersaturation attainable is very great, with others very slight. If the degree of supersaturation is increased (*e.g.* by cooling the solution of a substance, the solubility of which increases with temperature), a point is reached at which the solid separates spontaneously. We may then differentiate between a metastable region, following the stable region of saturation, and a labile region of greater supersaturation (p. 69). It is very difficult to fix the boundary between these regions, as it has been shown to depend not only on the nature of the substances but also on the presence of foreign solids (dust) in a manner not yet known; none the less "metastable limits" have lately been experimentally proved to exist (Miers 1906, Hartley 1907).



Sulphates.
Fig. 40.

Temperature Effect.—The effect of temperature on the solubility of solids in liquids is, as a rule, very considerable. The connexion is commonly shown by a graph, temperatures on the horizontal axis, and the concentration of the saturated solutions on the vertical axis. Solubility curves mostly ascend, *i.e.* in most cases the solubility increases with rise of temperature. A number of solubility curves are shown in Fig. 40, the concentrations being the weight of solid in 100 parts (by weight) of water. A very large number of investigations have been made, but they relate almost entirely to the solubility of salts in water. Owing to the partial dissociation of dissolved salts into ions this case is the most complicated of all; this may account for the few vague generalisations between solubility and other properties of substances which have been discovered.

As a first approximation it may be said that chemical similarity conduces to solubility. Thus, among organic substances, hydroxyl compounds as a class have the greatest solubility in water, and the solubility is greater the more hydroxyl groups are present. Increase in number of carbon or halogen atoms diminishes the solubility in water. Further, there is a definite connexion between solubility and melting-point; among isomeric compounds the compound with the lowest melting-point has the greatest solubility in any one solvent.

A further relation is that the solubility of comparable compounds in the sense of the periodic law increases or decreases with the combining weight. But this is merely a rough approximation.

Breaks.—An important feature of solubility curves is their continuity. So long as the nature of the solid remains the same, the solubility curve has no break or discontinuity. Conversely, it is certain that, if a solubility curve has a break, the nature of the solid phase has undergone a sudden change. This change may be due to polymorphism, fusion, combination with the solvent, or change in a state of combination; all these affect the continuity of the curve.

Each form of the solid substance has its own solubility. This best expresses the above phenomena. At temperatures where two different forms of the solid can coexist in contact with the solution, their solubilities must be the same, otherwise a perpetuum mobile of the second kind would be possible. The two solubility curves must intersect at this point. As one of the two forms is unstable outside this point it is unstable also in presence of the solution. But it is often possible to exceed the point, so that the actual intersection of several solubility curves has been experimentally verified.

The best-known example of this is sodium sulphate, the solubility of which is represented by the curve in Fig. 41, given by Gay-Lussac. The curve marked 10 is that for Glauber's salt (Na_2SO_4, $10H_2O$), that marked 0 is the curve for the anhydrous salt. At 33° the former

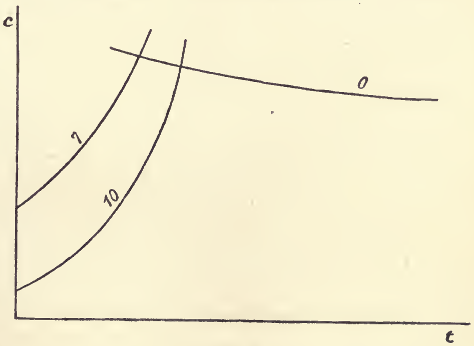


FIG. 41.

salt turns into a saturated solution in contact with the anhydrous salt, and from this point the solubility is that of the latter salt. But if all nuclei of Glauber's salt are rigidly excluded, solutions can be obtained below 33° which are in equilibrium with the anhydrous salt; their composition is continuous with that of the solutions above 33°, as is shown in the figure by the continuation of the curve to the left of the intersection.

The curve 7 is the solubility curve of the salt with $7H_2O$ already mentioned (p. 328).

Heat of Solution.—As a rule, heat is absorbed when solids dissolve in liquids, but the reverse happens not infrequently. General regularities connecting heat of solution with other properties are scarcely known.

There is an important connexion between the heat of solution and the temperature coefficient of solubility, an increase of solubility occurring when heat is absorbed during solution at constant temperature. Substances which evolve heat are less soluble at higher temperatures. The formula representing this connexion is similar to that for the connexion between vapour pressure and heat of vaporisation (p. 79). This is due to the similarity of the two processes, since it is a change into the state of dilute solution, which is comparable with the gas state. If c is the concentration of the solution, and L the heat of solution (absorbed heat being reckoned positive), the equation is

$$d \lg c/dT = L/RT^2.$$

It differs from the vapour pressure formula in having the concentration c instead of the pressure p, because heat of solution is not quite comparable with ordinary heats of vaporisation, since no external work is performed by solution in a solvent, as is the case on vaporisation at any pressure. Detailed development of this requires higher mathematics.

It must be remembered, in using the formula, that it is deduced on the assumption that the simple laws of osmotic pressure hold for the solution. It is therefore not valid for concentrated solutions.

A further difficulty arises in the latter case, for the heat of solution is not independent of the concentration, as in dilute solutions, but varies with it. If successive amounts of ammonium nitrate are added to a quantity of water, the amount of heat absorbed is smaller the more salt has already been added. In some instances the sign is reversed; crystallised cupric chloride, for example, dissolves in water with absorption of heat, and in an almost saturated solution with evolution of heat.

Although the formula does not apply to concentrated solutions, the connexion between the sign of the heat of solution and of the temperature coefficient of solubility remains. But the heat of solution must be taken as that in an almost saturated solution, and not in pure water. The sign of this heat of solution can be ascertained by making a supersaturated solution of the substance in question, and bringing about a sudden separation of solid by introducing nuclei.

Pressure.—The effect of pressure on solubility is given by the rule that on raising the pressure the reaction takes place which produces a diminution of volume, or, in other words, the reaction which opposes the rise of pressure. In most cases the volume decreases when a little salt is dissolved in an almost saturated solution; in this case the solubility is increased by increased pressure. A few instances are known in which solution takes place with expansion (*e.g.* ammonium chloride in water); they separate out salt when a saturated solution is subjected at constant temperature to greater pressure.

As the volume changes are very slight the effect of pressure is extremely small, very large pressures being required to produce measurable changes in solubility. For pressures up to a few atmospheres the effect can be ignored, as it is far below the limit of analytical error.

Two Solids.—Hitherto we have not taken the possibility of changes in the solvent into consideration. It must be taken into account, however, for if the solubility curve is continued to lower temperatures, the solvent must at last pass into the solid condition. Dissolving a foreign substance in a liquid always lowers the freezing-point, but not to an unlimited extent.

At some temperature below the melting-point of the solvent, depending on the solubility of the substance added, the solvent will appear in the solid form. We then have two solid phases along with the solution; if we assume the system to be placed in a vacuum, the vapour will appear as the fourth phase, and, according to the phase rule, the state is absolutely fixed, as no degrees of freedom remain.[1]

The Eutectic Point.—There is thus for each pair of such mutually soluble substances a definite temperature at which the two solid forms and the solution coexist. This is called the cryohydric or eutectic point. Its position is given by the following considerations.

We start with the melting-point T_A of the pure substance A. A little B is added, both are melted, and only at a lower temperature, which sinks as B increases, can equilibrium be formed with A as solid phase in contact with solution. If we plot the ratio of A to B horizontally, the curve slopes to the left and below from T_A,

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[1] In the experiment, as ordinarily carried out, the system is under the pressure of the atmosphere. The results are barely different from those in a vacuum, since the effect of pressure on this equilibrium is very slight, owing to the very small volume change.

practically in a straight line, since the depression of the freezing-point is proportional to the concentration (p. 184).

The same holds for B; if the equilibrium temperatures of solutions of A in B are plotted in the same diagram, we obtain practically a straight line, running to the right and downwards from T_B.

The two solubility curves must intersect at a point K. This point is common to both curves, and represents the equilibrium between the solution and both the solids, *i.e.* is the eutectic point of the pair of substances.

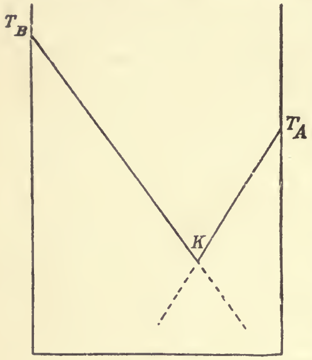

FIG. 42.

It is at once seen from the figure that the eutectic point lies further below the melting-points of the pure substances, the nearer the two melting-points are. Its position also depends on the slope of the two curves; this is given by L/T^2 in the formula given on p. 188, where L is the heat of fusion, and T is the melting-point.

If we retain the usual nomenclature, and denote the substance which is present as solid in presence of a saturated solution as the solute, and the other as the solvent, the curve to the right (T_AK) represents the solubility of A in B, *i.e.* the substance present in larger amount appears as the solute, and the small additions as solvent. This contradiction to our usual representation indicates that it is not desirable to make any such distinction between the two components. As a matter of fact, there is no scientific justification for the distinction, and it is better to speak of the two components of a solution without putting one before the other.

These considerations show very clearly the behaviour of a solution on continued cooling. On cooling the solution, the saturation temperature for one of the components is reached (which one it is depends on the composition of the solution), and this begins to separate.[1] The solution then becomes more concentrated with respect to the other component, and the temperature falls. This continues until the eutectic point is reached; then both components separate out simultaneously. They separate out in the proportion in which they are present in the solution, or the equilibrium temperature would rise spontaneously, which is impossible. The temperature remains constant until the whole has become solid.

If the original composition of the solution is the same as the eutectic mixture, solidification cannot commence until the eutectic temperature is reached, and it will proceed from beginning to end

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[1] It is assumed in what follows that supersaturation does not occur, or is prevented by the addition of nuclei at the appropriate time.

at that temperature. This solid mixture will also melt completely at constant temperature; it behaves exactly like a single substance, and was at first mistaken for such. The cause is that the liquid phase has the same composition as the mixture of the two solids, which brings it under the definition of equilibrium of the first order. That it really is a mixture of solids, and not a chemical compound, is shown by the fact that all its properties are the sum of the properties of the components.

Supersaturation.—The processes of solidification of mixtures are complicated by supersaturation, which occurs more or less readily. This possibility is indicated in Fig. 42 by the continuation of the curves beyond the point of intersection. If it is not excluded, the system may be taken past the eutectic point some distance along its own curve, and the temperature falls below the eutectic point. Only when the labile region is reached, or when nuclei reach the liquid in some way, does the solid separate out. The temperature then rises to the eutectic point, the heat of fusion being liberated, but no higher.

Supersaturation in the reverse direction does not appear to occur on fusion, so the simple diagram is always followed. As cooling is so much more frequently resorted to, it could not be passed over without explanation.

Partial Solubility.—The phenomena described above occur when the two substances in the liquid state dissolve in all proportions. This is not always the case, partial solubility of the liquids being at least as common an occurrence. In these cases the solid melts under the solution, and the circumstances are more complicated.

This phenomenon may be regarded as an extension of the simpler case just discussed. One of the solubility curves of Fig. 42 for solid-liquid is intersected by a solubility curve of the type of Fig. 38 for the mutual solubility of two liquids. This is shown diagrammatically in Fig. 43.

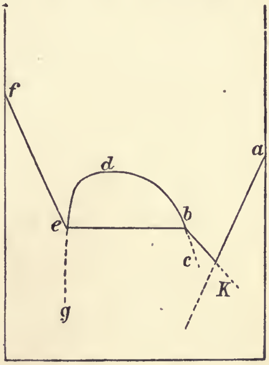

FIG. 43.

The portion aKb represents the ordinary solubility curves for two solids; in aK the one solid is present with the solution, in bK the other component is solid, and K is the eutectic point. But at b further addition of the second substance B (which in the figure is passing from right to left) gives rise to a second liquid solution, in which B predominates; there are then four phases: two liquids, solid B, and vapour. No degrees of freedom remain, and increase of B has no further effect on the composition of the phases or on the temperature. Further addition of B only produces an increase in the amount of the second solution and a decrease of the first, until at last at e the first solution disappears. When more B is now added an ordinary solubility curve for solid B and solution is obtained, which extends to f, the melting-point of pure B.

In the region eb we have equilibrium between two liquid phases. So long as solid B is present, the system follows the straight line eb; but if it is absent, a degree of freedom is gained, and the temperature can change. In this case the curve bde is obtained of the form shown in Fig. 38, p. 324, for the mutual solubility of two liquids. This curve does not necessarily end at b and e, but can be followed to lower temperatures, as indicated by the dotted prolongations bc and eg. This region is supersaturated for solid B.

Other Cases.—These indications by no means exhaust the subject, but merely illustrate the diverse nature of the questions that arise. Only one other relation will be mentioned; the two curves kb and bd, the former referring to the solid phase B and solution, the latter to a liquid phase in which B predominates, and the same solution, meet at an angle, which is fixed by the heat of fusion of B in the same way as the break in the vapour pressure curve at the melting-point of ice depends on its heat of fusion (p. 102). Solution of a solid in a liquid has many points of resemblance to vaporisation, and conclusions reached in the one region are easily applied to the other, with corresponding new results. These are so diverse in nature that their detailed study must be left to the larger text-books.

Solid Solutions.—From analogy there should be solid solutions in addition to gaseous and liquid solutions, *i.e.* substances which combine with the solid state the essential properties of solutions: continuous change in composition and in properties. Van't Hoff (1890) showed that a series of known phenomena could be classed together under the heading of solid solutions.

In the first place, mixtures of isomorphous crystals exhibit continuous alteration in composition and in properties. They are therefore examples of solid solutions. Along with isomorphous mixtures are ranged the not uncommon mixtures of two crystalline substances, which crystallise alone in different forms, but form uniform mixed crystals of the form of the predominant component. Naphthalin and naphthol, benzoic acid and salicylic acid belong to this group.

Then there are the cases where liquids or gases unite with solids in varying proportions to form solids, the properties of which vary continuously with the composition. The zeolites, natural hydrated silicates, are examples of liquid-solid combinations. The water can be removed to any desired extent from some of these, without destroying their homogeneous nature; they remain transparent, and the vapour pressure of water decreases with decrease in the amount of water they contain. The expelled water of crystallisation can be replaced by other liquids, such as alcohol, chloroform, carbon disulphide, etc., without impairing the transparency and homogeneous appearance.

The absorption of gases to form solid solutions is obviously not essentially different from that of liquids, as it is an accident of pressure whether water or chloroform is a liquid or a vapour. Gases which are difficult to liquefy have, as a rule, no great tendency to form solid solutions; there are striking exceptions, hydrogen-palladium being the best known. Iron also can form a solid solution with hydrogen, for when a vacuum is closed with an iron plate, which is then made a kathode in dilute acid, hydrogen is soon found in the vacuum. The gas dissolves in the iron and diffuses to the other side.

The essential difference between a solution and a mixture, namely, that work can be obtained by the preparation of a solution from its components, and that work is therefore necessary to separate the solution into its components, is reproduced in solid solutions. It is most easily shown in solid solutions of volatile substances. A dissolved substance must always have a smaller vapour pressure than the pure substance at the same temperature, for only thus is the above condition regarding work fulfilled.

The amount of this work is calculated in the following way: One mol of vapour is formed from the pure substance at constant temperature and at the normal vapour pressure p (the work = RT), the vapour is then allowed to expand with performance of work [the work = RT lg (p/p′)], until it has reached the pressure p′, at which it is in equilibrium with the solution. It is then absorbed by the solution (work = − RT). If p is the vapour pressure of the pure liquid, p′ that of the solution, the work gained in these three processes for one mol of solute is

$$RT + RT \lg (p/p') - RT = RT \lg (p/p').$$

The same amount of work must be done in order to separate the solution into its components.

The quantity of solution is assumed to be so great that the absorption of the vapour does not produce a measurable change in the concentration of the total solution, and with it a change in the vapour pressure. This assumption can always be supposed to be satisfied.

Such a diminution of vapour pressure has been actually observed in solid solutions, thus their nature as solutions is verified in this direction.

If this performance of work, or, in general terms, the diminution of chemical potential of the solute cannot be proved by direct vapour pressure determinations, it is usually possible to do so in some other indirect way, which is theoretically equivalent to it. The solubility in all solvents, the electromotive force in cells in which the solute is used up, etc., like the vapour pressure, must be smaller for the solution than for the pure substance. Judged by these criteria solid solutions have generally the characteristics of solutions.

Although there can be no question of the qualitative agreement, quantitative tests have not led to convincing results, for individual good cases are opposed by others which cannot be brought into line with them.

One Phase.—The most general case of equilibrium of the second order occurs when the two components unite in one single phase, in which they and the products of their interaction are in a state of homogeneous mixture or solution. If all the substances are gases, the problem of ascertaining the effect of temperature and pressure on the equilibrium can generally be solved. This can be done for liquids on the assumption that we are dealing with dilute solutions, that therefore the single substances form either the largest part or only a small part of the whole. The number of degrees of freedom is three; we have therefore to fix the temperature, the pressure, and a third variable, *e.g.* the concentration of one of the substances or the ratio of the two components, or (within certain limits) any other magnitude relating to the composition, and not till then is the system fully fixed, *i.e.* the concentrations of all the substances present known.

This diversity is reduced when the number of phases increases. With two phases two degrees of freedom remain, with three phases one only. These systems are similar in some respects to equilibria of the first order with the same degrees of freedom, and the analogies with them will be largely used to discover the laws which apply here.

A reaction leading to an equilibrium of the second order may in general be represented by a chemical equation as follows:

$$m_1A_1 + m_2A_2 = n_1B_1 + n_2B_2 + n_3B_3 + \;.\;.\;.$$

where A_1 and A_2 are the components, B_1, B_2, B_3, . . . the products and m_1, m_2, n_1, n_2, n_3, . . . the molar coefficients of the reaction. The number of different products which can be formed from the components and can coexist in equilibrium is theoretically unlimited. As a matter of fact, they seldom exceed two in number, frequently there is only one; and in other cases it is always possible to split up the equation into simpler ones. It will therefore be sufficient to take up these two cases.

As there is only one degree of freedom left in a one-phase two-component system after the pressure and temperature are fixed, the concentration of the different products which can result is not free, but, when one of them is fixed, all the others are fixed. There are relations between the concentrations of these substances which allow them, with one exception, to be eliminated from the equilibrium equation, reducing it to such a form that apparently there is only one product of reaction.

From the law of mass-action, the equilibrium equation for the case of a single product has the form:

$$a_1^{m_1} a_2^{m_2} = kb^n,$$

where a_1 and a_2 are the concentrations of the components, b that of the product, and m_1, m_2 and n are the molar coefficients of the reaction. The product of the concentrations of the components is therefore proportional to the concentration of the product, after each concentration has been raised to the power of its molar coefficient.

The equation can be deduced thermodynamically in exactly the same way as the gas equilibrium of the first order (p. 308), by making use of the principle of virtual alterations in energy. If the pressures corresponding to the concentrations a_1, a_2 and b, are denoted by p_1, p_2 and q, the virtual work is

$$m_1 RTd \lg p_1 + m_2 RTd \lg p_2 - nRTd \lg q,$$

and the condition that this value shall be zero leads to the equation $p_1^{m_1} p_2^{m_2} = rq^n$. The pressures are proportional to the concentrations, and thus the equation is identical with the one given above, $a_1^{m_1} a_2^{m_2} = kb^n$.

Illustration. — Hydrogen Iodide. — Hydrogen iodide affords an example of this kind of chemical equilibrium. It decomposes into hydrogen and iodine at temperatures about dull red heat, and is formed from them at the same temperatures. Both reactions are incomplete and lead to a chemical equilibrium represented by the equation $H_2 + I_2 = 2HI$. The equilibrium equation is $a_1 a_2 = kb^2$, from which the following behaviour can be predicted.

(*a*) The equilibrium is independent of the pressure or concentration. For the same factor is added to each concentration and therefore falls out of the equation. The ratio of the concentrations, and not their absolute value, is the factor for the equilibrium.

This is not the case in all equilibria of the second order, but only in those in which a common factor cancels out in the manner described. This occurs when the sum of the molar coefficients is the same on both sides of the equation, *i.e.* when $m_1 + m_2 = n$. This condition may be stated in this way: neither the pressure nor the volume of the gas mixture is changed by the reaction. It is readily intelligible, from the rules already given, that a reaction which does not alter the pressure is itself not affected by pressure.

This is fully borne out by the experiments on hydrogen iodide.

(*b*) The concentration of none of the substances can become zero. The more one of them is increased, *e.g.* hydrogen, the less there is of the other, *e.g.* of iodine, but they vary within finite limits.

(*c*) If a small quantity of iodine vapour is added to pure hydrogen it is not completely converted into hydrogen iodide, but only to an extent which depends on the value of k; so long as the amount added is small, the quantity of hydrogen iodide is proportional to the quantity of iodine. This is seen if the concentration of hydrogen in the equation is assumed to be constant.

(*d*) The equilibrium is not altered when the concentrations of iodine and of hydrogen are interchanged, since their product remains constant. This, too, is not always the case in equilibrium of the second order; it only occurs when $m_1 = m_2$.

(*e*) For the same total pressure the quantity of hydrogen iodide is greatest when the iodine and hydrogen are present in equivalent quantities. This is because the product of two factors, the sum of which is a constant, has the maximum value when the two factors are equal.

All these conclusions have been confirmed experimentally.

Other Examples.—The equilibrium between phosphorus trichloride, chlorine and phosphorus pentachloride is another case. The chemical equation is $PCl_3 + Cl_2 = PCl_5$, and the equilibrium equation is

$$a_1a_2 = kb.$$

In this case pressure does affect the equilibrium, for when all the concentrations are multiplied by a constant factor it does not cancel out, and the equation becomes incorrect. It is evident that if a_1 and a_2 are trebled, b must be increased ninefold to keep the equation correct. When the pressure is increased, therefore, the amount of the compound increases at the expense of the components, and conversely. As the volume is reduced to one-half by the formation of the compound from the components, it is clear that the reaction which occurs is the one that meets increased pressure with diminution of volume. If the space is enlarged, more of the components is formed; here, too, the pressure is not reduced so much as it would be, had no reaction taken place.

The earlier experiments on phosphorus pentachloride confirmed the above conclusions from the laws of equilibrium only in broad outline, but recent more accurate numerical tests have frequently been made.

If the components react with increase of volume, the behaviour would be the reverse of that described above; decomposition would increase when the pressure was raised, and diminution of pressure would favour formation of the compound. No case of this kind is known.

Temperature Effect.—The same considerations apply to the effect of temperature as were used in the corresponding cases of equilibrium of the first order. The work corresponding to the disappearance of m_1 and m_2 mols of components and the appearance of n mols of product is represented by

$$m_1RT(\lg p_1 - \lg p'_1) + m_2RT(\lg p_2 - \lg p'_2) - nRT(\lg q - \lg q'),$$

and the alteration in this work for a small displacement of temperature is $RTd \lg(p_1^{m_1}p_2^{m_2}/q^n)$. The expression in brackets is the equilibrium constant at the given pressure, and we again obtain the formula

$$d \lg r/dT = L/RT^2,$$

where L is the heat of reaction for complete transformation according to the chemical equation $m_1A_1 + m_2A_2 = nB$.

It is more plainly seen from this deduction than from that given on p. 309, that the same equation, $d \lg r/dT = L/RT^2$, is always obtained, whatever the number of components and the order of the reaction may be. In later cases it will not be necessary to deduce it at length.

The equation predicts, as formerly, that the equilibrium is displaced by rise of temperature in the direction of heat absorption, and the rise of temperature is less than if no reaction had taken place. This reaction is by no means necessarily the decomposition of a compound. In cyanogen, acetylene, ozone, nitric oxide, and other substances, we have compounds which contain more energy than the components. Accordingly, high temperatures do not favour decomposition of the compound as usual, but, on the contrary, increase the amount of the compound at the expense of the components. It has also been observed that at the highest attainable temperatures of the electric arc, carbon (which can here be regarded as a gas) readily unites with nitrogen and with hydrogen, forming cyanogen and acetylene respectively.

It is not theoretically or experimentally justifiable to assume, as is often done, that all compounds decompose at very high temperatures. The conventional deduction from the kinetic theory, that compound molecules must finally be split up into single atoms with rise of temperature, because the collisions become more and more violent, is in agreement with the current error, and in contradiction to both experiment and the rational theory of chemical equilibrium. So far no plausible explanation of this contradiction has been suggested.

The result obtained when $L = 0$ is worthy of notice. In general the heat of reaction changes with the temperature, and it can quite well happen that it passes through zero. Then $d \lg r = 0$, *i.e.* equilibrium will be independent of temperature at this point. If the heat of reaction changes in the usual manner with temperature, passing from positive values through zero to negative values (or in the reverse manner), r will first increase and then decrease (or the reverse), *i.e.* the equilibrium constant passes through a maximum (or minimum) value.

Hydrogen iodide appears to be an instance of this, but the measurements do not prove it with certainty.

Equilibrium in a Liquid Phase.—Liquids, as well as gases, can form one-phase equilibria of the second order. But all that remains of the quantitative laws is the qualitative relation between the change of conditions and the direction of the displacement of equilibrium. The form of the equations was obtained by calculating the work performed in the formation and disappearance of the components and their products; they cannot be calculated accurately except for perfect gases and dilute solutions.

Nitrogen peroxide is an illustration of the latter kind. It decomposes in solution in an indifferent solvent, such as chloroform, hexane, etc., into the simpler compound, as shown by the equation $N_2O_4 = 2NO_2$, and follows the same laws as if it were present in the state of gas (p. 306). But the coefficient k is not the same as for the gas, and it varies with the solvent; in general the degree of decomposition in the various solvents is much smaller than in the gas at the same concentration.

If the solution is not dilute, calculation of the coefficient k from the experimental data according to the simple mass-action equation does not give a constant value. The reason is that the concentration of the substances is no longer equal to the number of mols present divided by the total volume. The question, to what magnitude the significance of concentration is to be attached, must receive a different answer according to the circumstances. In many cases the concentration can be replaced by the "molar fraction," *i.e.* the ratio of mols of the given substance to the total number of mols in the mixture. This presupposes a knowledge of the molar weight in the liquid state, and this may not only be different from that of the same substance in the state of vapour, but varies with temperature and the nature of the other substances present.

Compounds with the Solvent.—Numerous and extensive investigations have been made in one special case of equilibrium in liquids, namely, where the solute decomposes into ions. As already stated (p. 192), this occurs when salts dissolve in water, and it is fairly probable that the ions do not consist of parts of the salt alone, but that the solvent water takes part in their formation; that the ions, therefore, are to be regarded as hydrates of the salt radicals. Ionic equilibrium will be fully dealt with later; all that will be said here concerning the above statement is that the question, whether ions are hydrates or not, can not be answered from the laws of dilute solutions. The molar fraction, $n/(n + N)$, which decides the lowering of vapour pressure and of the freezing-point, becomes $n/(N + n - m)$, if m mols of water are taken up by the n mols of solute, and are consequently withdrawn from the solvent. But owing to the assumption that the solution is dilute, this change in the molar fraction is so small as to be indistinguishable from the experimental errors. If we attempt to increase the effect by using more concentrated solutions, it is doubtful whether the simple laws still hold, and any irregularities which may be observed cannot with certainty be put down to the formation of hydrates.

As the same argument applies in all cases of combination between solvent and solute, it is very difficult to prove the existence of such compounds in the homogeneous solution, and our knowledge of them is very slight. The only indications, for it does not amount to proof, are the deviations from the additive scheme shown by solutions; the more the properties of the solution differ from the sum of the properties of the components, the more probable is the conclusion that chemical action has taken place between them.

The colours shown by iodine in various solvents is an illustration. In carbon disulphide and chloroform it forms a reddish violet solution; solutions in ether, petroleum and other liquids are brown in colour; further, the colour changes with the temperature. Molar weight determinations give the same molar weight, I_2, in both kinds of solutions; the most probable cause of the difference remaining is the formation of compounds between the iodine and the solvents. Closer investigation of other properties of such solutions might yield further information in this direction.

Concentrated Solutions.—The question now arises, how may the "active mass" be determined, *i.e.* the amount which represents the substance in the equilibrium equation, if the equation is to retain its form. A general method of determining this amount experimentally is the estimation of the partial pressure of the vapour of each substance in the mixture. From the law of substitution of one phase by another with which it is in equilibrium, or the equality of the chemical potential of the substances concerned in such equilibrium, the active mass in the liquid state must be replaceable by the concentration in the vapour, and the latter is an unambiguous measure of it.

It follows from this that the substances when present in the same ratio as in the vapour phase, as constituted from the solution according to the partial pressures, must also be in equilibrium, or a perpetuum mobile of the second kind could result. We further see that in dilute solutions the same equilibrium laws must apply, as in gases. For the concentrations in the solution are proportional to those in the gas or vapour (Henry's law, p. 315), and the simultaneous presence of other gases has no effect on this relation (Dalton's law).

The law of mass-action must apply to dilute solutions, just as for gases, the only difference being the introduction of constant factors, which are fixed by the solubility coefficients of the vapours in question.

From this point of view it is easy to specify in what cases the active mass in solutions of finite concentration can be put down as proportional to the molar fraction. This is permissible if the partial pressure of the vapour is equal to the pressure of the pure liquid, multiplied by the molar fraction. It has been already indicated in what cases an approximation to this has been observed.

The formula for the effect of temperature on equilibrium in a liquid system loses its numerical value when the concentrations of the liquids are finite. But, since it can be empirically established that the active mass of a substance always increases and decreases at the same time as the concentration or the molar fraction, the rule that at higher temperatures the reaction takes place which absorbs heat can still be shown to be true.

One Solid Phase and a Gas.—The simplest two-phase equilibrium of the second order is that between one solid phase and a gas. Except in the comparatively uncommon case of solid solutions (p. 334), the solid can be regarded as of constant composition. Consequently, the partial pressure of its vapour will depend only on the temperature; and in a vapour phase, which is in equilibrium with the solid, the concentration of this component at a given temperature can have only one value. Its concentration can therefore be replaced in the isothermal equation by a constant, the expression being simplified by this process.

Consider the simplest case, the reaction $m_1A_1 + m_2A_2 = nB$; there are two possibilities. Either one of the components, A_1 or A_2, or the compound B can be present in the solid form. The form of the equilibrium equation differs in the two cases; introducing the constant concentration into the coefficient k, we have the two equations:

$$a^m = kb^n, \text{ and } a_1^{m_1}a_2^{m_2} = k.$$

In the first the powers of the concentrations of the variables are directly proportional; in the second they are inversely proportional or their product is a constant.

The second case has been more thoroughly investigated than the other. The ammonium compounds of many gaseous acids are instances of two gases uniting to form a solid compound. The laws relating to these cases were first tested experimentally and confirmed on these substances (ammonium hydrosulphide, ammonium carbonate, etc.) by Isambert (1881).

Ammonium hydrosulphide will serve as an illustration; it is formed from equal mols of ammonia and hydrogen sulphide according to the equation

$$NH_3 + H_2S = NH_4HS.$$

In the equilibrium equation the two exponents m are equal to unity, and its form is

$$a_1a_2 = k.$$

By suitably changing the constants the concentrations can be replaced by the partial pressures, which can be measured directly, the equation becoming $p_1p_2 = r$. From it the following conclusions may be drawn.

If neither gas is in excess in the vapour, p_1 always remains equal to p_2. From this, equilibrium must result at a fixed pressure, $p = \sqrt{p_1p_2} = \sqrt{r}$; thus the solid, although the gas it sends out is a mixture, behaves like a single substance, with a vapour pressure varying only with the temperature. This can be arrived at from another point of view. The assumption is made that the gas phase has the same composition as the solid; this is the definition of equilibrium of the first order, and under this condition the system must behave like one of the first order. This has been so fully confirmed by observation that it was a little difficult to realise at first that the results would be different when the gases were not in equivalent amounts.

This "dissociation pressure" varies with the temperature, and increases with rise of temperature just as vapour pressures do. The formula is $d \lg p/dT = L/RT^2$, in which L is the heat of formation of the solid from the gases. The justification for treating the reaction as one of the first order indicates the proof of this equation.

If the two gases are present in the gas phase in different amounts, the total pressure is not comparable to that of a single substance; it is greater and varies with the volume even when the temperature is kept constant. This follows from the following consideration.

If the volume is diminished at constant temperature, part of the gases separate out as solid compound. Equal volumes of the gases disappear, and the ratio of the two becomes more unequal the smaller the total volume. The total pressure is $p_1 + p_2$; according to the law of mass-action the product p_1p_2 is constant. But the sum of the two factors of a constant product is greater the more unequal the factors are; the total pressure is greater the smaller the total volume is made for any given excess of one gas. The equation is symmetrical for the two components, *i.e.* equal excess of either component has the same effect on the total pressure.

If, on the contrary, the volume is increased, the total pressure diminishes; its limit is $\sqrt{r}$ for equal amounts of the two components.

Ammonium carbamate differs in some respects from the hydrosulphide. It is formed from two volumes of ammonia and one H carbon dioxide, the chemical equation being $2NH_3 + CO_2 = NH_4CON$ of and the equilibrium equation $a_1^2a_2 = k$. The concentrations of the two components are not symmetrical; if the ammonia concentration is doubled, that of carbon dioxide will fall to a quarter, in order to preserve equilibrium.

This was foreseen theoretically before it had been observed; it was confirmed by an investigation specially directed to that end (Horstmann, 1873).

The relations developed above retain their validity whether the vapour pressure of the (undecomposed) solid is measurable or not, *i.e.* whether it is present in measurable amount in the vapour phase. In most of the cases investigated it is not present in appreciable amount; the vapour does not contain sufficient of the compound to be detected by the density (which for the above compounds is respectively 2 and 1·5 times as great as for the mixture of components).

Notwithstanding this, it is more rational to assume the presence of the compound in the vapour, for the reasons already given (p. 325). There is no independent ascertainable difference between the cases in which a finite vapour pressure has been observed and the others; the limitation is rather one of our analytical methods, and is therefore not final. On the other hand, the theoretical assumption that all substances are volatile to a definite extent, even though it is often excessively small, has not led to any consequent contradiction of observation, so that it may confidently be used in further applications.

When a gas acts upon a solid with formation of a second gas the circumstances are different. The case of nickel carbonyl, $Ni(CO)_4$, has been fully investigated; the phenomena to be expected can easily be predicted with certainty. Let us imagine, for illustration, that a metal unites with chlorine to form a volatile chloride, which at the given temperature partially decomposes again into its components, so that equilibrium occurs. The chemical equation is $2Me + nCl_2 = 2MeCl_n$, and the equilibrium equation is $a^n = kb^2$. In this case an increase of pressure of one gas will cause an increase of pressure of the other gas. If $n = 2$, the ratio of the two pressures remains constant; if n is different from 2 the ratio changes, but they increase or decrease simultaneously.

Two Solid Phases and a Gas.—The case is still simpler if two solid phases appear. To this group belong the chemical equilibria of heterogeneous systems, which formerly were studied under the name of dissociation. It was a fuller knowledge of dissociation which finally dispelled the view, at one time prevalent, that chemical reactions were always complete.

The laws governing this equilibrium are obtained from the general formula by making two of the concentrations constant. It is obviously of no consequence which of the values of the typical equation $a_1^{m_1} a_2^{m_2} = kb^n$ they are, for the equation in any case becomes $a = K$, *i.e.* there is only one variable concentration; or in the language of the phase rule, three phases and one degree of freedom.

Such a system behaves like a volatile single substance; there is only one equilibrium concentration or pressure possible for each temperature, and this is independent of the amounts of the substances. The essential difference between the two cases is that two solid phases are necessary to fix the equilibrium, and that the equilibrium is indefinite if only one is present. This important point is frequently overlooked, and even at the present day we find researches on the decomposition pressures of such systems, in which the question, what are the two solid phases, is unasked and unanswered.

One of the earliest cases investigated is the decomposition of calcium carbonate into calcium oxide and carbon dioxide. The solid phases are calcium oxide and calcium carbonate, carbon dioxide is the gas phase, and Debray (1867) showed that the decomposition gives rise to a "dissociation pressure" which has a fixed value for each temperature. If the pressure is greater than this, gas is absorbed by the calcium oxide, until the normal pressure is reached: if it is smaller, calcium carbonate decomposes until the normal pressure is reproduced.

It has since been found that the matter is not so simple as Debray thought it to be: in particular, a subcarbonate seems to be formed, and this introduces another constant in the equilibrium. This has been proved to occur with barium carbonate.

Another much studied example is found in the efflorescence of salt hydrates. Mitscherlich (1844) measured the vapour pressure of efflorescing Glauber's salt, and it is clear that he regarded it as purely a temperature function. This was first expressly stated as a law by Wiedemann and Debray (1866 and 1868), who made experiments to establish it. Later, fairly extensive investigations have shown that the amounts of the solid phase really have no effect on the pressure; and that the pressure of a partly effloresced salt hydrate varies only with the temperature.

It was for a long time overlooked that the nature of the effloresced product has as important an effect on the vapour pressure as has the original hydrate. Different pressures are obtained when the same hydrate forms different effloresced products.

Calcium chloride is an example of this important rule. It usually crystallises with $6H_2O$; there are, further, two different hydrates with $4H_2O$, one being an unstable form with respect to the other. The vapour pressures of the hexahydrate are different, according as it has effloresced to one or other of the tetrahydrates; it is greater with the more stable hydrate.

The latter seems to be in contradiction to the generalisation that the vapour pressure of the more unstable compound is greater than that of the more stable (p. 104). The contradiction disappears on closer inquiry into the process. Suppose the two systems, the hexahydrate with the stable tetrahydrate, and the hexahydrate with the unstable tetrahydrate, placed in the same space; water will distil from the region of greater vapour pressure to that of less, *i.e.* from the stable to the unstable hydrate. Consequently, in the former system a part of the hexahydrate will be turned into the stable tetrahydrate, and in the latter an equivalent amount of the unstable tetrahydrate will pass into the hexahydrate. The result is that the unstable form will diminish, and the stable form will increase, the total quantity of hexahydrate remaining the same. This is exactly what would be expected; it would also happen if the two systems were brought into direct contact.

Other cases in this group are the ammonia compounds of many salts (*e.g.* of metallic chlorides), which easily dissociate into the salt and ammonia. The equilibrium here, too, is dependent only on the temperature; the amounts of the two solid phases have no effect on it, but any change in the nature of a solid phase alters it.

The effect of temperature on the dissociation pressure is directly connected with the heat of formation of the compound. As there is only one variable component in the gas phase, the formula simplifies to the vapour pressure formula of a homogeneous substance. If L is the heat of fixation of one mol of water vapour by the effloresced product with formation of the higher hydrate, the equation (p. 79) is $d \lg p/dT = L/RT^2$. Subtracting the corresponding equation for water, the pressure being denoted by p_w, $d \lg p_w/dT = W/RT^2$, in which W is the heat of liquefaction of one mol of water vapour at the same temperature, we have $d \lg(p/p_w)/dT = (L - W)/RT^2$. The difference $L - W$ is no other than the heat of combination of liquid water with the effloresced product, and as this is the magnitude usually determined, the equation affords a direct comparison with the observed results.

Measurements of the vapour pressures of a number of partially dehydrated salts at different temperatures, and thermochemical determinations of the heats of hydration enable us to test the equation. Owing to the inaccuracy of the earlier measurements the calculations gave results which were so contradictory that they seemed to disprove rather than confirm the theory, but later investigations (Frowein, 1887) with more refined methods of measuring vapour pressures brilliantly confirmed the theory.

The behaviour of salt hydrates on exposure to air is now easily explained from what has been stated above. As is well known, some effloresce at room temperature (Glauber's salt), while others (borax) usually retain their water of crystallisation, but effloresce in some circumstances. Others, again (nickel sulphate), do not effloresce at all at room temperature.

The explanation is as follows: air is not usually saturated with moisture, but contains only ·6 or ·7 of the water vapour, which could be present at the temperature. Accordingly, all hydrates which in contact with the effloresced product give a relative vapour pressure of over ·7, will lose water and effloresce; if the vapour pressure is much below ·6 they will remain uneffloresced, and if the relative vapour pressure lies about the limit, they will do one or the other according to circumstances.

If a pure, unbroken crystal of a salt hydrate is placed in an atmosphere, the pressure of water vapour in which is below the dissociation pressure, efflorescence will not necessarily take place; supersaturation can take place here, as in so many cases. So long as the second solid phase, the effloresced product, is absent, the vapour pressure is not fixed and can vary within certain limits (within the metastable region, p. 69). Thus, undamaged crystals of Glauber's salt can remain uneffloresced in air of ordinary dryness for any length of time if the access of nuclei is prevented. If efflorescence commences at any point, the direct effect of contact with the new phase is shown by the spreading of the efflorescence in a regular manner from the place. The region of efflorescence is a sphere, a uniaxial or a triaxial ellipsoid, according to the crystal system, just as in the case of the surface of optical elasticity, though, of course, the constants are not the same.

Liquid and Gas.—The simplest equilibria of the second order between liquids and gases have been dealt with already; they conform to Henry's law, the concentrations in the two phases being in a constant ratio. The question still remains as to gases, which on solution partially undergo chemical change.

This change consists in interaction with the solvent, and may be represented by the equation $m_1A_1 + m_2A_2 = nB$. To calculate the final state, we assume that Henry's law holds only for the unchanged part of the solute, the changed part as such having no effect. The "partition law," that the partition of a substance between two phases of variable concentration is independent of the presence of other substances, has been stated in isolated cases by various investigators; its present comprehensive form is due to Nernst (1891).

If the concentration of the unchanged part of the solute is a_1, that of the solvent a_2, and of the product b, the equilibrium equation corresponding to the above chemical equation is $a_1^{m_1}a_2^{m_2} = kb^n$. The solution is assumed to be dilute, the concentration of the solvent is therefore constant, and the constant $k/a_2^{m_2}$ can be replaced by K; the equation thus becomes $a^m = Kb^n$.

If $m = n$, *i.e.* if one mol of compound is formed from each mol of gas, the concentration of the unchanged portion is always proportional to that of the combined part. In this case Henry's law still holds, for the total amount of gas absorbed is also proportional to the unchanged part, and the only effect is that the solubility is greater by the amount which has entered into combination.

If m is not $= n$, there is not proportionality between the changed and the unchanged parts, and Henry's law cannot hold. An easy calculation, which is left to the reader, shows that, if $m > n$, the apparent solubility (*i.e.* the total amount of gas dissolved, divided by the pressure) increases with increase of pressure, while in the contrary case ($m < n$), it decreases with rise of pressure.

Cases of this kind of equilibrium have been frequently investigated, but no example has been found which gives simple, calculable results.

The influence of chemical action on solubility is very strikingly shown by the halogen acids. They are, as is well known, very soluble in water with strong evolution of heat: the heat amounts to much more than the heat of liquefaction of the pure gases, so that heat is also evolved, if the liquefied halogen acids are dissolved in water. The boiling-point is at first raised by the solution of the gas, reaches a maximum and then falls again. The vapour pressure at constant temperature follows the opposite course. According to the rule given on p. 322, dilute solutions of these acids must become more concentrated on distillation, mainly water passing over into the distillate; very concentrated solutions, on the other hand, will lose acid, and become more dilute. Between them is a concentration (for hydrochloric acid it is 20 per cent) at which the vapour has the same composition as the residue, and the solution distils unchanged. That it is not a chemical compound, as is sometimes erroneously supposed even yet, was demonstrated by Roscoe (1860), who found that this composition varies with the pressure, from 18 per cent at 180 cm. to 23 per cent at 5 cm. pressure. The vapour density, too, is that of a mixture of hydrogen chloride and water vapour.

The chemical reaction in this case consists essentially in the formation of hydrogen ion and halide ion from the compound. As this increases the number of mols, the apparent solubility must, according to the theory given above, diminish with rise of pressure. This is markedly the case, for the greater part of the gas is absorbed at very small pressures, and an increase of pressure is accompanied by a comparatively inconsiderable increase in the quantity dissolved.

Liquid and Solid.—There is little to add to what has been already said about the equilibrium between a solid and a liquid phase. The general relations deduced from the phase rule are regulated by the number of components, and not by the number of compounds formed from them. The circumstance, that such have been formed, is absolutely without influence on the general position, and, conversely, no information can be got in this way regarding the existence of such compounds. For this reason the question, what compounds are to be supposed to be present in a given solution, has been satisfactorily answered in very few cases.

Solubility is always increased by chemical action between the solvent and the solute. For when equilibrium is finally established, it is between the solid phase and the unaltered part of the same substance in the solution. The apparent solubility is so much greater than the actual solubility the more it has passed into other compounds. The chemically altered part has the same effect on the true solubility as any other foreign substance; if in small amount its influence is not great, if otherwise, its effect is to change the nature of the solvent.

These considerations are especially applicable in the most fully investigated case of aqueous solutions. It is now certain that in them only a part of the salt is dissolved unaltered; the greater part is decomposed into ions, and to this circumstance is due, in large measure, the general solubility of salts in water.

If we are in a position to determine or estimate the solubility of the unaltered substance, the excess found by experiment over this estimated amount is a measure of the chemical reactions which have taken place. It gives no suggestions as to their nature; for this other methods, which cannot be further specified here, must be resorted to.

Solid Compounds.—If the newly formed substances separate out as solids at the temperature, there are produced characteristic changes in the form of the typical melting-point curve with a eutectic point (Fig. 42, p. 332). A compound AB formed from A and B has its own melting-point, and this can only be lowered by the addition of other substances. If there is a fusible compound anywhere in the series comprising varying amounts of A and B, it will be shown by a maximum melting-point, which will be lower on both sides, *i.e.* for more A or more B than the compound contains. Such a compound existing in the solid state is characterised on the fusion diagram by a maximum or summit.

Such maxima have been observed in these cases; they are sometimes peaked, sometimes rounded; we must inquire on what the difference depends. It depends on the condition of the liquid or fused mass; if this consists of the undecomposed compound AB a peaked maximum is formed; if it is partially decomposed the maximum is rounded off, and is flatter the more decomposed the compound is.

In the former case the liquid consists of the pure compound AB, and addition of A or B has the same effect as an entirely different substance, causing at first a straight-line depression of the melting-point. We have, therefore, at the melting-point of AB two fusion curves meeting at a definite angle. But, if the liquid is partially decomposed, it already contains both A and B, although it was made from pure AB, and addition of A or B does not introduce any new substance, but merely increases the concentration of one already present. The point corresponding to AB in the fusion curve is only a point on a continuous curve representing a continuous change in a state, *i.e.* the curve has a rounded peak which is flatter, the more the fused liquid has decomposed. Rounded maxima are the predominant type in the cases which have been investigated; the compounds seem, therefore, usually to undergo partial decomposition on fusion. The theoretical limiting case and the average conditions actually met with are both shown in Fig. 44.

If A and B combine in several proportions to form solid compounds, it need hardly be said that the same considerations are repeated. Each compound has a maximum, between them the fusion curves intersect at the eutectic points, which are minima in the curves. By determination of the melting-points of all mixtures of A and B (in practice, of a sufficient number of mixtures), we can find out the number and the composition of the solid fusible compounds, which can be formed from A and B. Investigations of this kind have been of very great service, especially in the chemistry of alloys. This method possesses a great advantage over the ordinary method based on the isolation and separate examination of the specific properties of possible compounds, in that isolation is not necessary. The existence of the compound and its composition are recognisable from the fusion curve, and the pure substance can be obtained at once by fusing together the components in the right proportions (if necessary, they are calculated more exactly from the combining weights).

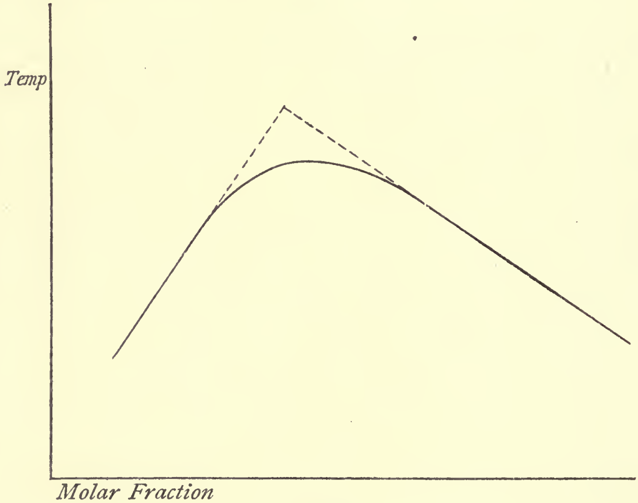

FIG. 44.

Partial Fusion.—In addition to the compounds which melt to a liquid of the same composition, as described above, there are other compounds, which decompose at a fixed temperature into another solid phase and a liquid, the composition of which is not the same as either of the solids. Glauber's salt ($Na_2SO_4,10H_2O$) is an example of this. It decomposes at 32·5° into anhydrous salt and a saturated solution of sodium sulphate, which is in equilibrium at this temperature with both the hydrated and the anhydrous salts. Here the sum of one solid phase and the liquid phase is equal to the other solid phase (anhydrous salt + solution = Glauber's salt), and not, as in a eutectic point, the composition of the liquid the same as the two solid phases together. The composition of the liquid lies outside that of the two solid phases, and, in consequence, a transition point of this kind does not represent a maximum or minimum temperature, but produces only a discontinuity or break in the direction of the fusion curve. The position of the break marks the composition of the solid compound concerned.

The Complete Fusion Curve.—The complete fusion curve of a binary system is accordingly made up of single curves, in which three kinds of singular points are distinguishable. First, temperature minima, representing eutectic points between bordering solid phases. Secondly, summits or temperature maxima, representing the existence and composition of such compounds as melt completely, *i.e.* can pass into a liquid of the same composition. Thirdly, breaks, in which two curves, running in the same sense, intersect at a definite angle; they mark the existence and composition of compounds which decompose on heating into another solid compound (or one of the components) and a liquid of different composition.

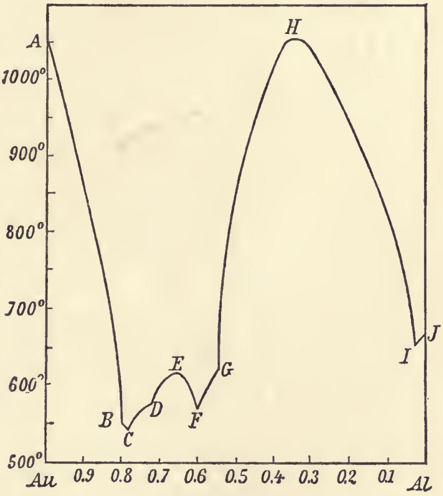

FIG. 45.

As an illustration of all these features the complete fusion curve for the system, gold-aluminium, is reproduced in Fig. 45. At E and H we have fusible compounds with ·33 and ·67 Au, corresponding to the formulæ Al_2Au and $AlAu_2$. There are breaks at B, D and G, which point to the existence of other solid compounds. Finally, C, F and I are eutectic points.

Three Phases.—If three phases are present in a system of the second order, there is one degree of freedom only, and the relation between pressure and temperature follows the general equation $dp/dT = W/Tu$ (see p. 79). If there is no gas phase, *i.e.* only liquids and solids are present, the volume changes, u, which can occur, are very small, while the heats of reaction, W, have about the usual values. The ratio dp/dT is thus very large, just as in the simple case of water and ice, previously explained, and very large pressures are necessary to produce slight alterations of the equilibrium temperature. In most cases the alteration is barely noticeable, and, except in special circumstances which permit considerable rise in pressure, these condensed equilibria appear to be associated with a perfectly fixed temperature. An instance is the common practice of fixing the zero of thermometers by means of melting ice; the temperature really does vary with pressure, but to so small an extent that the differences of pressure caused either by changes of barometric pressure, or of the hydrostatic pressure of the ice-water mixture, are of no account, even in fine measurements. Equilibrium points of the second order may be utilised for fixing temperatures, as has long been the practice with similar equilibria of the first order.

An investigation on Glauber's salt, directed to this end, has shown that extremely constant temperatures can be realised in this manner, and that the method can be as successfully applied to determining fixed points as the melting-points of pure substances, *e.g.* of water. The temperature is affected by foreign substances in the same way as ordinary melting-points; still it has been found possible, with comparatively simple purification, to obtain a fixed point with Glauber's salt which is accurate to ·001°. The temperature is 32·484° on the international scale, or 32·379° on the hydrogen scale (Richards, 1898).

On the other hand, if a gas or vapour phase is present, the system behaves like the vapour in contact with a liquid or solid phase in equilibria of the first order, *i.e.* there is a definite vapour pressure for each temperature (and conversely). The differences are, firstly, that two liquid or solid phases are necessary for equilibrium, and secondly, that the liquid phase varies with the temperature, not only in pressure or concentration, but generally also in composition.

The Quadruple Point.—In a two-component system, four phases must be present if the system has no degrees of freedom left. This gives a "quadruple point," corresponding to a triple point in equilibria of the first order (p. 100). We have such a point, for instance, when a vapour phase is added to the above system of sodium sulphate decahydrate, anhydrous salt, and saturated solution. It differs from the "condensed" triple point, in that not only the temperature but also the pressure is absolutely fixed, and that neither of these can be displaced in the slightest without a phase disappearing.

From the four phases of the quadruple point, four combinations of three phases can be formed, namely, abc, abd, acd and bcd, if a, b, c, d, are the four phases. Each of these three-phase systems has one freedom, and gives a temperature-pressure curve. If one of the phases present is vapour, three of these curves have the character of vapour pressure or dissociation curves, since each phase, therefore also the vapour phase, comes in three of the combinations. The fourth curve then represents a condensed system. If a vapour phase is not present, the curves belong to condensed systems, and run almost parallel to the pressure axis.

To every quadruple point belong four sets of states, each with one degree of freedom, represented by four temperature-pressure curves. These four curves must meet in one point, the quadruple point.

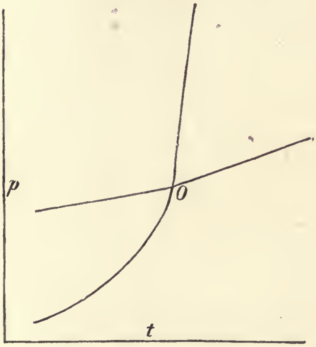

Fig. 46.

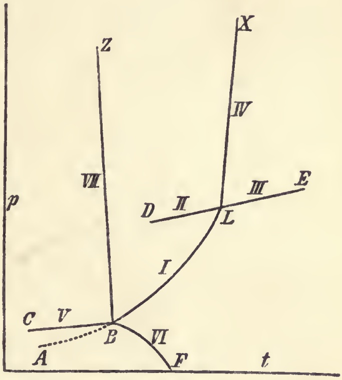

Fig. 47.

At the place where any two of these curves intersect the two sets of phases must be in equilibrium; as each set contains three phases, and the two sets are different, all four phases must be present at the point of intersection of two curves, and must be in equilibrium. Since the intersection of each of the remaining curves with one of these again gives rise to an equilibrium between the same four phases, all four curves must have the same point of intersection, and be in a position similar to O in Fig. 46.

Four is the largest number of phases in a two-component system which can be in equilibrium together. But it is possible to have from two components more than four different compounds or solutions; in general, more than four phases can exist. The question arises, What happens when the number of possible phases is greater than four?

The answer is, that several quadruple points result, connected by the curve representing the three phases which are common to two quadruple points. In this manner, any number of forms and compounds can be brought in, and many cases are known already in which this occurs.

As an illustration we will take the first case which was fully investigated from this point of view, the compounds of sulphur dioxide with water (Roozeboom, 1885). The possible phases are—

a. Solid hydrate $SO_2, 7H_2O$.
b. Liquid solution of SO_2 in water.
c. Liquid solution of water in SO_2.
d. Gaseous solution of SO_2 and water vapour.
e. Ice.

In the point L (Fig. 47) the phases are a, b, c, d; at B they are a, b, d, e. The connecting curve I represents the equilibrium of the phases common to L and B, a, b, d. The other curves represent the following three-phase systems: II = a, c, d; III = b, c, d; IV = a, b, c; V = a, d, e; VI = b, d, e; VII = a, b, e.

CHAPTER XIV

CHEMICAL EQUILIBRIUM OF THE THIRD AND HIGHER ORDER

The Chemical Equation.—While there is only one form of chemical equation for equilibria of the second order, viz. $mA + nB = A_mB_n$, there are two possible forms in reactions of the third order, and this gives rise to some differences. We may have $mA + nB + pC = A_mB_nC_p$, and $mA + nB = pC + qD$. In the former one new compound is formed from three components, in the latter two new substances are formed from two components.

The former case is easily recognisable as a reaction of the third order, but one might be inclined to put down the latter as of the fourth order, as four different substances are present. In consequence of the conservation of elements the composition of D is fixed if A, B, C are given, for it must be represented by $mA + nB - pC = qD$. It is a matter of choice which of the four substances is taken to be conditioned by the other three, for a similar equation holds for each one; but the number of independent components is not variable. It amounts to three. In ascertaining the order of reaction, and the number of components for the application of the phase rule, only independent components are to be counted, *i.e.* the number of relations between the composition of the substances must be subtracted from the total number of substances. The number of degrees of freedom can increase only with the number of independent variables, here the components.

Another difference is that the simplest case, namely when three components A, B and C form only solutions and not compounds, is found only among the first class of equations. It is frequently difficult to decide, in a given case, whether a compound is formed or not.

The first type of reaction is known as addition reactions; the second as substitutions or double decompositions.

Components.—As previously stated, the choice of components in any given system is more or less arbitrary, especially if negative quantities are admitted. But the number of independent components, which can represent the composition of the whole system and of every phase, remains fixed. There are often phases in which only a small number of components are recognisable. As the limit of recognition is variable and is being constantly displaced by improved methods, a want of definiteness is introduced, but, obviously, this has no effect upon the fundamental question. The number of components is therefore the smallest required to compose all the phases which occur.

All doubt on this matter can be avoided by asking how many phases within the region under consideration are necessary to make up any one of them, arbitrarily chosen. In equilibria of the first order, any phase present can be prepared from any other. In equilibria of the second order, in general two phases are required to make up any other, etc. In this connexion, the phases are not only those which can coexist, but all the phases in any part of the whole system under consideration. For instance, the equilibrium between water vapour and iron, in which hydrogen and iron oxide are formed, might be supposed to be of the second order, as two substances are brought into reaction. But the solid phase iron oxide which is formed cannot be represented in any way as the sum or difference of the two other phases, iron and water vapour + hydrogen. This is only possible if another phase, pure water or hydrogen, or, generally, a second gas phase of different composition, is brought in. The equilibrium is thus one of the third order.

On the other hand, the equilibrium between gold and aluminium, described on p. 351, is of the second order, although five different pure substances are formed. But every solid phase in this system can be represented as the sum of the two pure substances (which occur as phases in the two extreme fusion curves) or as the sum or difference of any two compound phases, when they are taken in the right proportion. For if a is the ratio of the compound in one phase, and b in another, any desired ratio c can be represented by the expression $c = a \pm kb$, where k is the arbitrary ratio in which the two phases are united. It is essential that in these cases the chemical reactions can be carried out, that therefore the expression $a \pm kb$ denotes an actual chemical process. If this were not the case the equilibrium would be of higher order, corresponding to the number of compounds of A and B, which are not convertible into each other. Such a case occurs in the case of hydrocarbons.

Graphic Representation.—The complexity of equilibrium of the third order compels us to select a number of typical cases for consideration, without any attempt to exhaust every conceivable possibility. We shall first, following the treatment of reactions of the second order, consider cases of simple solution. As the equilibrium between solid and liquid phases (complete mutual solubility of the liquid phases being assumed) is the simplest, we shall take that up first of all. To obtain a comprehensive view by means of diagrams, we must seek a convenient co-ordinate system.

The simplest method of expressing the composition of a ternary system is to divide the amount of each component by the total amount of the system, which gives the amount as the fraction of the whole. If A, B and C are the actual amounts of the components, the fractions are:

$$a = \frac{A}{A + B + C}, \quad b = \frac{B}{A + B + C}, \quad c = \frac{C}{A + B + C},$$

so that $A + B + C = 1$. The amounts may be expressed either in parts by weight, or, more conveniently, in mols, *i.e.* parts by weight divided by the molar weight.

If the side of an equilateral triangle be taken as unity, any point in the interior has the property that the sum of the three parallels to the sides, drawn through the point to the sides, is always equal to unity (to the side of the triangle). Accordingly, all possible ratios of three components can be represented by points within an equilateral triangle, just as all the possible ratios of two components can be represented by points on a straight line of unit length.

The apices of the triangle represent the pure substances, the three sides the binary systems of two of the components, and the interior of the triangle the ternary systems.

Fusion of Ternary Mixtures.—The simplest case of equilibrium of the third order is the fusion of mixtures of three solids, which in the liquid state dissolve in each other in all proportions. We will suppose the eutectic mixtures for the three binary mixtures, AB, AC and BC, to be known; they are K_3, K_2 and K_1 in Fig. 48. Some C is added to the fused eutectic of AB, which is in equilibrium with solid A and solid B. This will lower the temperature; at the same time the proportion of A to B in the liquid will be changed a little, until it is again in equilibrium with solid A and solid B. The point which now represents the composition of the liquid lies inside the triangle near K_3, say at i. With further addition of C the point recedes within the triangle, and these points, which represent equilibrium with the two solid phases A and B, form an almost straight line, running in the direction of K. The solution will at last become saturated with C, and a point is reached at which it is in equilibrium with all three solids.

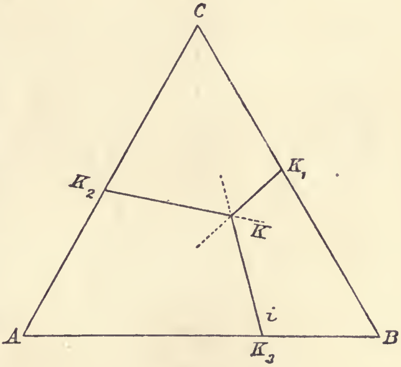

Fig. 48.

The same will happen if we commence with the eutectic mixture of A and C and add B to it. We shall obtain a curve which runs from K_2 towards K and intersects the first curve at K. As the equilibrium is the same as before, namely, solution and the three solids, the point K must be common to both curves, *i.e.* is the point of intersection.

The same considerations apply to the eutectic mixture of B and C. Its curve also must pass through K, and, as is shown in Fig. 48, the three curves of equilibrium with two solid phases and solution intersect in the point K, which is the ternary eutectic point. It lies, as is clear from the above discussion, at a lower temperature than any of the binary eutectic points, but has otherwise the same properties as them. In particular it is the lowest temperature at which the liquid phase can be formed from the three components, and as the composition of the liquid cannot alter during solidification, the temperature remains the same until all the liquid has become solid.

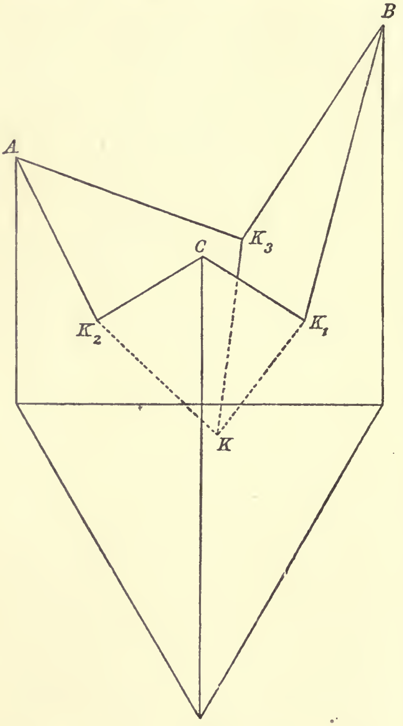

FIG. 49.

These conclusions have been fully confirmed.

Fig. 48 does not show the temperature changes. To do this, an axis must be added normal to the plane of the diagram, and the temperatures plotted on this. The three lines, then, are arranged in space and form the edges of a triangular prism.

Fig. 49 illustrates this. The three peaks, A, B and C are the melting-points of the pure substances; the three binary eutectic points K_1, K_2 and K_3 appear on the three sides of the prism, and from these start the three curves of the ternary mixture, which intersect at the ternary eutectic point K. The solutions in equilibrium with one solid phase lie on the surfaces AK_2K_3K, BK_3K_1K and CK_1K_2K, and those which are in equilibrium with two solid phases are on the lines K_1K, K_2K, K_3K.

To represent this on a plane diagram, use is made of isothermals, or lines of equal temperature. These surround the ternary eutectic temperature K in the shape of irregular triangles, each higher temperature represented by a larger triangle. The angles of the triangles are on the lines K_1K, etc.; at temperatures above the lowest binary eutectic point the triangles are incomplete, so that in the vicinity of the single melting-points from within there only remain approximately parallel portions of a side.

In Fig. 50 are shown in this manner the results of Charpy's experiments (1898) on the alloys of lead, tin and bismuth. The isothermals are 25° apart.

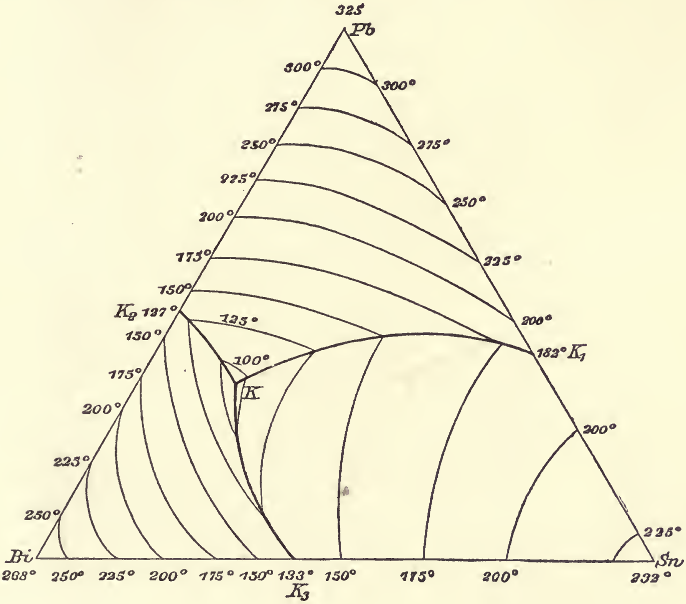

Fig. 50.

Ternary Liquid Solutions.—The various types of mutual solubility, complete, partial or vanishingly small, of different liquids, already encountered in equilibrium of the second order, naturally recur in the present case. The number of possible combinations is much greater, for each of the three pairs of liquids, AB, AC and BC, can belong to any one of these three types, giving rise to ten different combinations. This is the number of differences which can occur on the three sides of the triangular diagram on p. 357; to these must be added the variations in the interior, *i.e.* the behaviour of the ternary solutions, which may form one, two or three coexistent liquid phases, according to their character.

As the development of all these possible cases lies far beyond the scope of this book, only a few typical examples will be taken up in detail. But the opportunity may be taken to point out that the phase rule enables us to treat this branch of chemistry deductively. That is, without an experiment being made, all the possible cases can be developed from the laws of combination, and systematically represented. The problem then is to find out how far all these cases can be realised experimentally, thus testing or confirming the theoretical premisses. Sometimes it is found that only certain groups of the predicted cases can be realised; then the expressions regulating this limitation have to be ascertained.

We have such a restriction, for instance, in the fact that the number of coexistent phases is limited by the state of aggregation. First of all, there is never more than one gas phase, as all gases are miscible in all proportions. The number of liquid phases has never been found to exceed the number of independent components (liquid crystals are counted as solid phases). The number of solid phases is unlimited so far as is known.

Not more than three liquid phases, then, are to be expected in equilibria of the third order. The most general case, in a certain sense, is that in which the three pairs of two components each are partially miscible, and form in certain proportions three immiscible solutions. Fig. 51 illustrates this case.

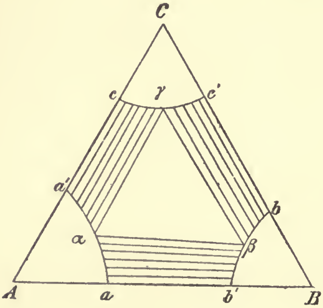

Fig. 51.

Let us consider first all combinations of A and B. If a little B is added to A, a solution will be formed, according to the assumption, until saturation is reached at a, when a second liquid phase of the composition b′ separates. All compositions between a and b′ produce these two saturated solutions of constant composition, and complete solution is not obtained again until B is in large excess, between b′ and B. The other pairs BC and AC behave similarly.

If now increasing amounts of C are added to the different solutions of A and B, what happens depends upon the composition. It is obvious for geometrical reasons that when C is added to any solution of A and B, that the composition of the resulting ternary mixtures lies on the straight line which joins C and the point on AB representing the original solution. Only for points on this line does the ratio of A to B remain unchanged, as is seen at once on drawing the co-ordinates.

If C is added within Aa, there results at first a single ternary solution. The same holds for b′B. But between a and b′, each of the two immiscible liquid phases takes up some C; its composition is then expressed by a point in the interior, situated on aα or bβ. To every point of the first line there corresponds one on the second; this connexion is denoted on the diagram by tie-lines. The ties are not necessarily parallel to the sides of the triangle (or to each other).

Extending these considerations to the other two pairs, we find that at the three apices are homogeneous regions, all three components being present in each solution. Between them are three regions, like ab′$\beta\alpha$, in each of which two liquid phases coexist. The question now is, what happens when so much C is added to the middle solutions of AB that the line $\alpha\beta$ is passed.

Such a quantity of C is greater than can be taken up by the two liquid phases, in one of which A preponderates, and B in the other. A third liquid phase will be formed, consisting mainly of C. Its composition is given by the point γ.

There are still two degrees of freedom, according to the phase rule. If these are disposed of by fixing the temperature and pressure, each of the three liquid phases must have a fixed composition, which is independent of the ratio of A : B : C (within the whole region in which the three phases are formed). This region is denoted by the triangle $\alpha\beta\gamma$.

There are therefore three kinds of regions within the triangle. First, at the three corners are the fields, in which only one liquid phase is present. Between these, around the sides, are three regions, each with two liquid phases, and finally, in the middle is a triangular field with three liquid phases. While the composition of the phases varies within the appropriate limits, in the first two regions, it is constant in the three-phase region. Whatever the composition of the system may be within this region, it always forms three liquids, the composition of which is always the same, provided the temperature and pressure are constant. This obviously corresponds to the case of the binary solutions of two partially miscible liquids, the liquid phases of which have a constant composition within a certain region. In both cases an alteration in the relative amounts of the components causes merely a change in the relative amounts of the three phases.

It is not difficult, after this explanation, to develop the cases in which the mutual solubility of one or of two pairs of liquids is zero. The corresponding one-phase regions at the corners, and the two-phase side regions recede to the edge. The system assumes a new character when pairs of completely soluble liquids are present.

Critical Points.—A well-known case of this kind is water, alcohol and ether. Water and alcohol are completely miscible, and so are alcohol and ether, but water and ether are only partially miscible. As is well known, alcohol acts on the mixture of water and ether, or, more correctly, on the two mutually saturated solutions, so as to increase the mutual solubility, until at last complete solution takes place.

This is represented diagrammatically in Fig. 52, in which W is water, A is alcohol, and E is ether. The real difference between this case and the former is that the addition of alcohol makes the two solutions a and b more alike, so that the corresponding lines continuously approach, until they coincide at a point k. While up to this point there were two liquid phases, a single additional drop of alcohol is sufficient to make them the same and uniform.

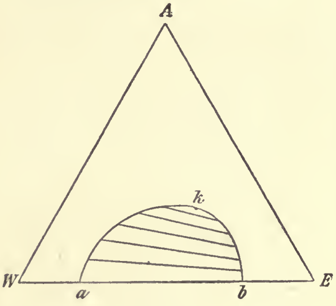

Fig. 52.

Similar cases, in which two hitherto different phases steadily approach equality and finally become equal, have been already met with. The equilibrium of the first order between a liquid and its vapour ended with increasing temperature in the critical point, at which the two phases lost their difference. There was, further, the equilibrium of the second order, where the mutual solubility of two partially miscible liquids increased with rise of temperature. Here, too (p. 324), the phases became more alike, and at last became identical, the two merging into one. This differs from the previous case in there being still a degree of freedom left, so that the critical point is displaced a little by pressure. For one degree of freedom is left, since two phases are present in a two-component system, with the condition that the phases are to be identical.

In the present case of ternary equilibrium two degrees of freedom remain, *i.e.* the composition at the critical point varies with temperature and pressure. Such critical points are obviously possible in equilibrium of any other order; the general definition is as follows: a critical point is one at which two phases become identical.

To obtain such a critical point experimentally we commence with the partially miscible liquids (ether and water) in any proportion, and add the third (alcohol) little by little. As the first two liquids are probably not in the right proportion, the one phase will increase at the expense of the other. If this is the water layer, for example, ether must be added, until the two phases are present in about equal amount, and the additions of alcohol continued. The inequality of the amounts of two phases is corrected as before, and by alternate additions of the necessary component and of alcohol, we reach a point where a single drop of alcohol suddenly causes the two phases to unite. If the three components were taken from stocks of known weight, the weights of the amounts used give the composition at the critical point.

Vapour Pressures of Ternary Mixtures.—The numerous types of equilibrium between liquid and vapour, already seen in reactions of the second order, are again met with in the case of ternary mixtures. We will consider first the case of complete miscibility, starting from the binary solutions represented by the three sides of the triangular diagram, each of which can give one of the three possible types 1, 3, and 5, of vapour pressure curve (p. 322). If we imagine the vapour pressures to be plotted on an axis normal to the horizontally placed triangle, a triangular prism is obtained, closed above by a curved surface. This surface represents the vapour pressures of all possible ternary mixtures. The vapour pressure surface is bounded at the three sides of the prism by the vapour pressure curves of the corresponding binary solutions. We shall consider only one of the many possible types.

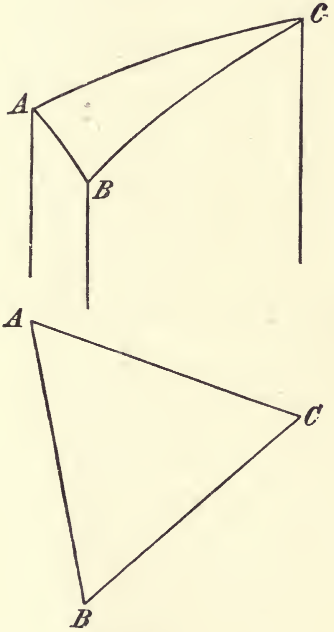

Fig. 53.

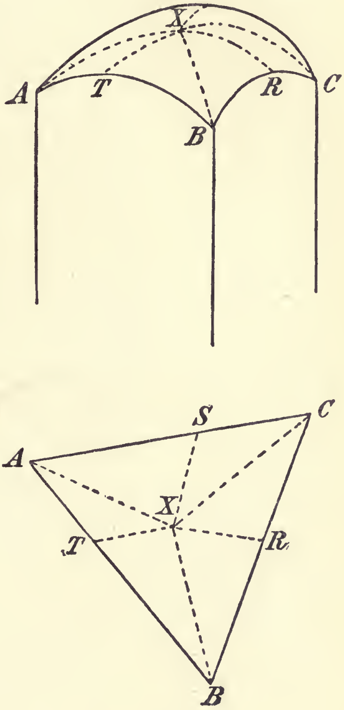

Fig. 54.

If the three binary vapour pressure curves have no maximum or minimum, the ternary vapour pressure surface will have the appearance shown in Fig. 53, *i.e.* it will also rise or fall unilaterally, and will have no singular point. Considerations, similar to those given on p. 322, point to the conclusion that such a ternary mixture can be separated into its components by repeated fractional distillation.

If, on the contrary, all three boundary curves have a maximum, the surface is dome-shaped, Fig. 54, with a maximum point X. There is then a ternary solution with a greater vapour pressure than any other solution; it is also greater than the maximum vapour pressure of the binary solutions. Fractional distillation will not yield the pure substances in this case, but in general, one component in the pure state, then a binary solution with a maximum vapour pressure, and finally the ternary solution, mentioned above, with the vapour pressure maximum X. Which of the three components, and which of the binary solutions is obtained depends on the position of the original ternary mixture in the triangle. The whole triangle is divided into six fields, the boundaries of which run on the one side from the apices to the principal maximum point X in the interior (Fig. 54) and on the other, from the three binary maximum points situated on the sides of the triangle to the same point X. These six fields of the ternary solutions correspond to the two parts into which, in the case of binary solutions with a vapour pressure maximum, this point divides the composition curve, so that each of these halves characterises the solutions from which, on fractional distillation, the solution with the greatest vapour pressure and the one or other pure component are obtained.

The case in which the vapour pressure surface is bounded by three binary curves, each of which has a vapour pressure minimum, can be treated in a similar manner.

In addition to these types there are of course many different combinations of the three binary curves, but they cannot be gone into here.

Limited Solubility.—The complications are much greater when the three liquids are not, as previously assumed, mutually soluble in all proportions. Some idea of the possibilities can be got from a consideration of the typical case represented in Fig. 51 (p. 360). We will assume, as a further simplification, that the binary vapour pressure curves are as shown in Fig. 54 (p. 363).

Then the vapour pressure in the one-phase corner fields at A, B, C, will behave as already described (Fig. 54), *i.e.* each point corresponds to a particular vapour pressure, and the whole of these pressures is represented by the corresponding parts of the dome-shaped vapour pressure surface.

In the two-phase side regions the composition of the two phases remains constant along the tie-lines of corresponding points, only the relative amounts of the two phases undergoing change. Accordingly, the vapour pressure along such a tie-line must remain constant, *i.e.* in the vapour pressure surface to every such line there corresponds a horizontal straight line. Each group of these horizontal lines forms a horizontal cylindrical surface.

In the middle three-phase region there are always three liquid phases of constant composition. The corresponding vapour pressure surface is a horizontal plane, for the vapour pressure is here independent of the total composition, since there are always the same three liquid phases, only in different amounts.

The complete vapour pressure surface is shown in Fig. 55; it is obtained from the dome of Fig. 54 by first cutting off the summit horizontally, then three curved cuts are made towards the sides with a knife, whose edge is kept in a horizontal position. This corresponds exactly to the simpler case of binary solutions, in which the vapour pressure curve of incomplete solubility is derived from the curve of complete solubility, its crown being cut off by a horizontal straight line, which corresponds to the two-phase region.

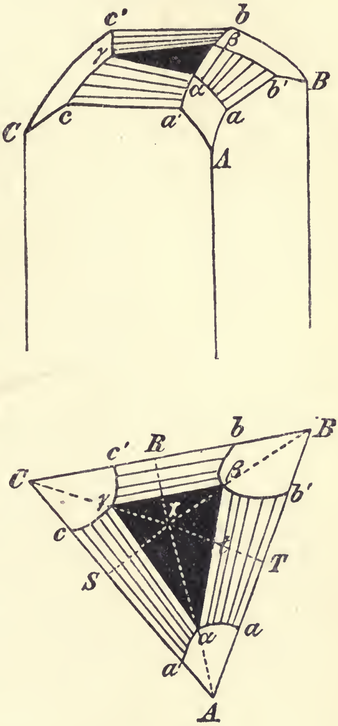

Fig. 55.

Equilibrium of Higher Order.—We now turn from the purely formal treatment of the phase rule to a quantitative examination of the equilibrium in individual uniform phases. As may be recollected from the earlier simple cases, there are regular relations between the concentrations of the different substances to be taken into account.

The general formula for isothermal equilibrium between any number of components can be deduced in a manner similar to that in which the formulae for equilibrium of the first and second order were found. If the chemical equation is

$$m_1A_1 + m_2A_2 + m_3A_3 + \ . \ . \ . \ = n_1B_1 + n_2B_2 + n_3B_3 + \ . \ . \ . \ ,$$

the work for a small displacement of equilibrium—all the components supposed to be gases—is given by

$$RTd\ \lg[(p_1^{m_1}p_2^{m_2}p_3^{m_3}\ .\ .\ .)/(q_1^{n_1}q_2^{n_2}q_3^{n_3}\ .\ .\ .)].$$

The condition that the sum of the works is zero, is given by $p_1^{m_1}p_2^{m_2}p_3^{m_3}\ .\ .\ .\ = k.q_1^{n_1}q_2^{n_2}q_3^{n_3}.\ .\ .$, a quite general equation for any number of substances which obey the gas laws, and are in equilibrium at constant temperature.

The general formula for the effect of temperature, $d \lg k/dT = L/RT^2$, also applies, L being the amount of heat taken up during the complete course of the reaction expressed by the equation.

If there are solid phases, the equation is simplified, because for each solid phase one of the factors p or q becomes constant. If a reaction is of the nth order and n solid phases are present, there is only one degree of freedom, as the total number of phases with the gas phase is $n + 1$, and there is an equilibrium pressure, like a vapour pressure, which depends only on the temperature. In particular, the composition of the gas phase is fixed for each temperature, however complex its composition may be. If the temperature is changed, the pressure and the composition of the gas phase both alter.

If the number of solid phases is $n - 1$, the degrees of freedom are 2, and the composition of the gas phase can change at constant temperature; but only in such a manner that one estimation fixes all the others. The relations here are very similar to those developed on p. 342.

If one of the phases is liquid, the systems generally lose their simplicity, and no general representation has yet been found for the complex conditions which take its place. Only in the fairly frequent instances in which one of the components[1] in the liquid phase is in great preponderance, do we find simpler conditions, owing to the validity of the laws of dilute solutions, and the consequent applicability of the general equilibrium relations.

The rule to be followed in such cases is to set down the active mass of the predominant substance or solvent as a constant, while the gas laws apply to the substances present in small quantity, the pressure being osmotic pressure. Of course, any number of solid phases can still occur; their treatment has already been indicated.

The Mutual Relation of Chemical Equilibria.—This rule applies to the simplest form of chemical equations. There may be forms, according to which different products are formed at the same time from the same original substances. Such equations can always be split up into simple equations, of which they are the sum, and the rule applies to these single equations.

Each such simple equation leads to an equilibrium equation between the powers of the concentrations or active masses of the reagents; this equation contains one coefficient, which is usually also a function of the temperature. A compound equation contains

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[1] The predominant substance may be a compound of several components, without formally altering the state of affairs. For any compound of the simpler components may be regarded as a component from the equilibrium point of view, if we admit calculations with negative quantities. This cannot lead to error, if care is taken that these negative quantities do not fall below the possible values, which are fixed by the total composition of the whole system.

as many coefficients as the number of simple equations composing it. Generally the compound equation can be split up into simple ones in several ways; then the number of simple equations comprised in it is the smallest number, the sum of which make up the compound one. There are as many numerical relations between the coefficients of the various simple equations as will lead to the given number of independent coefficients according to the rule.

For example, the equation

$$2CaCO_3 + H_2O = Ca(OH)_2 + CaO + 2CO_2$$

contains five different substances, and should therefore be a reaction of the fourth order. But it can be resolved into the single equations $CaCO_3 + H_2O = Ca(OH)_2 + CO_2$, and $CaCO_3 = CaO + CO_2$, the former of which is of the third order, the latter of the second order.

If one equation is subtracted from the other, we obtain $Ca(OH)_2 = CaO + H_2O$, representing the decomposition of calcium hydroxide into calcium oxide and water. This equation is not independent of the others, and its equilibrium coefficient must be a function of the other coefficients. If the partial pressures or active masses of the individual substances be denoted as follows: $CaCO_3 = a$, $H_2O = b$, $Ca(OH)_2 = c$, $CO_2 = d$, $CaO = e$, — the equations $CaCO_3 + H_2O = Ca(OH)_2 + CO_2$, and $CaCO_3 = CaO + CO_2$, give the equilibrium equations $ab/cd = k$, and $a/de = r$, where k and r are the equilibrium constants. By division we have $c/be = r/k$; this equation represents the equilibrium of $Ca(OH)_2 = CaO + H_2O$, and its coefficient is the quotient of the other two coefficients.

We thus arrive at the remarkable result that equilibrium states between substances can be calculated without direct investigation of the particular reaction. In the present example we can calculate the equilibrium between calcium oxide and water vapour, if we know the decomposition of calcium carbonate by water vapour, on the one hand, and its dissociation into calcium oxide and carbon dioxide, on the other. This possibility depends on the fact that the corresponding chemical equations can be combined, and this is always the case, when the different equations contain the same substances partially. For each new chemical equation, which is obtained by the elimination of such common members, necessarily represents a conceivable reaction which can be carried out, at least indirectly.

The number of components for a given equilibrium is fixed by the kind of chemical reaction under consideration, and the number of components in the same system can vary if the reaction changes. Thus, the common changes of state of water come under equilibrium of the first order; but if the temperature is raised to 2000°, water decomposes into hydrogen and oxygen, and the equilibrium is then of the second order.

Equilibrium of the Third Order.—If these generalisations are applied to equilibrium of the third order, two typical forms of equilibrium equation are obtained, corresponding to the two typical forms of chemical equation

$$p_1^{m_1}p_2^{m_2}p_3^{m_3} = kq^n$$

and

$$p_1^{m_1}p_2^{m_2} = kq_1^{n_1}q_2^{n_2}$$

the first of which holds for addition reactions, the second for double decompositions.

According to the explanation already given of dependent and independent components, these equations show that when all the components are present in a phase in variable proportions, three of them are independent; the fourth concentration is fixed, when three of them have been arbitrarily fixed. This most general case is restricted when a phase of constant concentration (*e.g.* a solid which does not form solid solutions) enters the system. For when one of the concentrations is constant in one of the phases in equilibrium, the concentration of this substance must also be constant in all the other phases, which are in equilibrium with it.

This rule, which has been fully established by experiment, is the general law of intensity applied to chemistry. Just as in all the phases which take part in the reaction, the temperature and pressure must have the same value, so, too, the chemical intensity or potential must have the same value in all such "coexistent" phases, each substance present with its own value. As the chemical potential is proportional to the concentration at constant total pressure and temperature, the concentration must be constant in all the phases, when it is kept constant in one.

It follows from this that if several phases of variable concentration are in equilibrium, there is an equilibrium equation for each phase, but that the coefficients of these equations cannot be independent of each other, being so related that the available number of degrees of freedom is not exceeded. How this is brought about is more easily seen under certain simple experimental conditions, to which we will pass at once.

Examples.—There are so many different types of equilibrium of the third order, that it is impracticable to mention all the possible types. It will be sufficient to select a number of examples, which merit special attention either because of their general nature, or because of the importance of the reaction.

The reaction between iron and water vapour is an example of equilibrium of the third order in which a gas phase and solid phases are present. The products of the action are ferrosoferric oxide and hydrogen. The chemical equation is

$$4H_2O + 3Fe = 4H_2 + Fe_3O_4,$$

and as two solid phases and a gas phase are present, there are two degrees of freedom. If the temperature and total pressure are fixed, one partial pressure can still be arbitrarily chosen, but the other is then fixed.

This is evident if the pressure of water is denoted by p, and that of hydrogen by q, and the other constant factors are combined with the equilibrium constant; the equation is then $p^4 = kq^4$, or $p = Kq$, *i.e.* the pressure of hydrogen must be proportional to that of the water vapour.

Further, it follows from the thermochemical data that the reaction of water vapour on iron evolves heat, 34 kj. for one mol of hydrogen. It must therefore regress with rise of temperature.

The formula is confirmed beyond doubt by the observations of Deville (1870), who neither expected this relation nor deduced it from his observations. The equilibrium is displaced by fall of temperature in the direction of hydrogen, as heat is evolved by its formation. This is confirmed by the work of Preuner (1904).

Water Gas.—A technically important equilibrium of the third order is the double decomposition between carbon monoxide and water vapour, hydrogen and carbon dioxide, represented by the equation

$$H_2O + CO = H_2 + CO_2.$$

The elements carbon, hydrogen, and oxygen may be taken as the components; if we prefer components which are actually present, we may take any three of the four gases, since the chemical composition of the fourth can always be represented as the sum of the other three (with negative terms, if necessary).

If we denote the pressures of the four substances by p_1, p_2, q_1, q_2, the formula is $p_1p_2 = kq_1q_2$. As there are three components and one phase, there are four degrees of freedom, *i.e.* two partial pressures, the total pressure, and temperature may be arbitrarily fixed. The total pressure has no effect on the equilibrium in this case, as there is no volume change during the reaction (or because a common factor of all the pressures cancels out of the equation).

Horstmann (1877) showed that the observed results agree in the main outline with the theory. The observations were necessarily limited to the equilibrium which results when mixtures of carbon monoxide and hydrogen with insufficient amounts of oxygen were exploded. As the highest temperature lasts only a very short time, one cannot be certain that equilibrium has been established; and, further, it will be displaced by the fall in temperature. Horstmann's results were confirmed by a later research of O. Hahn (1903), who measured the stable equilibrium. The constant K_H of the equilibrium $\frac{(CO)\cdot(H_2O)}{(CO_2)\cdot(H_2)}$ has the value ·84 at 786°, and 1·6 at 1000°.[1]

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[1] The concentrations of substances are frequently expressed, as here, by enclosing the formula of the substance in brackets.

The conversion of hydrogen and carbon dioxide into water vapour and carbon monoxide absorbs heat; it is a reaction which must progress as the temperature is raised. Conversely, more hydrogen will be formed the lower the temperature is at which equilibrium has been established. This fact is of importance in the manufacture of "water gas," which is the product of the action of water vapour on coal at a high temperature. The reaction at high temperatures is mainly $H_2O + C = CO + H_2$. From the above discussion it is obvious that at lower temperatures the reaction will be mainly $2H_2O + C = 2H_2 + CO_2$. As the use of water gas is largely increasing, it is important to know that the amount of the poisonous carbon monoxide can be restricted in favour of the formation of hydrogen by carrying on the process at the lowest possible temperature (Mond, 1897).

In examining theoretically the processes involved in the formation of water gas, *i.e.* in the presence of solid carbon, we have to observe that in the ratio $\frac{(CO) \cdot (H_2O)}{(CO_2) \cdot (H_2)}$, the first quotient, $\frac{(CO)}{(CO_2)}$, is fixed by the equilibrium between solid carbon and its two oxides, which is in a high degree a function of the temperature. While at 550° the gas is almost entirely carbon dioxide (with only 10 per cent carbon monoxide), at 800° the gas is 90 per cent carbon monoxide and 10 per cent dioxide. From the chemical equation

$$CO_2 + C = 2CO$$

we get the following equilibrium equation, as (C) goes into the constant:

$$\frac{(CO_2)}{(CO)^2} = K_O,$$

which, in combination with the above equation K_H for the equilibrium investigated by Horstmann, enables us to calculate the water gas equilibrium.

If the equations are multiplied together (CO_2) disappears, and we obtain

$$\frac{(H_2O)}{(H_2)(CO)} = K_H \cdot K_O,$$

which is the equilibrium equation of the reaction

$$H_2O + C = H_2 + CO.$$

If, on the contrary, the first equation is squared, and then multiplied by the second, we have

$$\frac{(H_2O)^2}{(CO_2)(H_2)^2} = K^2_H \cdot K_O,$$

which is the equilibrium equation of the other reaction

$$2H_2O + C = CO_2 + 2H_2.$$

The two last equations are therefore not independent, but are defined by the two equations of the Horstmann reaction and the equilibrium between carbon monoxide and carbon dioxide. The water gas equilibrium can be calculated, without a single direct experiment being made, if the two equilibrium constants K_H and K_O as functions of the temperature (even only numerically, not in the shape of a complete expression) are known; conversely, if all the concentrations in a water gas equilibrium are known, the constants K_H and K_O of the two fundamental equations can be calculated for the given temperature. For the carbon monoxide—carbon dioxide equilibrium, we only need to substitute the measured concentrations of CO and CO_2 in the equilibrium equation $\frac{(CO_2)}{(CO)^2} = K_O$, in order to calculate the constant; similarly, the concentrations of the four gases give the constant K_H of Horstmann's reaction, of which the equilibrium under consideration is only a special case (viz. in the presence of solid carbon).

It may be added that at temperatures of about 1000° at which water gas is usually made, the equilibrium concentration of carbon dioxide is very small, less than 1 per cent at atmospheric pressure. In actual practice equilibrium is not usually reached, and as carbon dioxide is first formed in preponderating amount as the most unstable compound under the prevailing conditions, the composition of the gas differs from the theoretical composition in the direction of excess of carbon dioxide. The more rapidly the reaction is finished, *i.e.* the quicker the gases are withdrawn from contact with the glowing carbon, the greater the amount of carbon dioxide.

Solutions.—If two different substances are dissolved in a third, which is in large excess, the laws of dilute solutions apply to the two former, and the equilibrium is in many respects very similar to those of the second order. The third substance or solvent then plays the part of space, in which are the two others; it must not be forgotten, however, that its influence on the numerical values of the equilibrium constants is very considerable. Different solvents do not by any means produce the same equilibrium state with the same solutes at the same volume. This specific influence of the solvent is comparable with that of temperature, so that different solvents at the same volume act as if the solute was in the same space, but at very different temperatures. Or, better still perhaps, volume-coefficients may be ascribed to the different solvents, such as, for example, 2 ccm. of one solvent have the same effect as 1000 ccm. of another.

In consequence of the similarity between solution and vaporisation, equilibrium of the second order with a gas phase is reproduced in the third order, the vacuum being replaced by a solvent, and a solute taking the place of the vapour. Accordingly, the circumstance that the solvent may have united with the other components or compounds of them, is without influence on the form of the law, provided it is present in so large excess that the solution may be regarded as dilute.

We have then to assign a limit to dilute solutions. It depends to some extent on the nature of the substances; but it may be taken for granted that solutions which contain less than 1/10 mol per litre can without hesitation be regarded as dilute. Stronger solutions than this can often be regarded as dilute, but the precaution should be taken of applying special tests before applying the simple laws of solution to them.

The first case is the homogeneous equilibrium between two components in a solution. The equation given on p. 337 applies here, $a_1^{m_1}a_2^{m_2} = kb^n$; all the relations developed there are reproduced here.

More well-investigated examples of this type of equilibrium are known than for all other types put together, as the decompositions of binary electrolytes into ions is governed by this equation (Ostwald, 1888). Ionic equilibrium is dealt with later, and the mere reference will suffice here.

If a solid phase is present along with the liquid phase, the relations developed on p. 342 apply. The solid may either be a compound, in which case the product of the powers of the concentrations of its components must be constant (*i.e.* a function of the temperature only), or the solid may be a component, and then the two variable (powers of the) concentrations must be proportional to each other. Solutions of electrolytes afford numerous instances of the former case; the latter, for which the simpler type has not yet been observed, may be illustrated by the following example (Noyes and Seidensticker, 1898).

Iodine is very sparingly soluble in water, but if a soluble iodide is added to the water, the solubility increases very much. The reason is that iodine adds itself to the iodide ion, forming tri-iodide ion of the formula I_3'. The equation is $I' + I_2 = I_3'$. Iodine will dissolve until the amount of free iodine in equilibrium with tri-iodide ion is the same as the solubility of iodine in pure water; the assumption is made that the solvent suffers no extensive change, *i.e.* the solution remains dilute.

In the equilibrium equation $a_1 a_2 = kb$, the concentration of free iodine, a_2, is a constant; a_1 and b are then proportional, *i.e.* the amount of tri-iodide ion should be in a constant ratio to the amount of iodide ion. Potassium iodide solutions were saturated with solid iodine at 25°, the iodine taken up titrated, and the iodine simply dissolved subtracted from this amount. The simple solubility in pure water was directly determined, and was found to be ·001342 mol (or 1·342 millimol) in a litre.

KI taken.	Iodine dissolved (corr).$=I_3'$.	I'.	Ratio I_3'/I.
106·3	53·94	52·4	1·03
53·15	26·69	26·46	1·01
26·57	13·34	13·62	1·02
13·29	6·66	6·63	1·01
6·643	3·325	3·118	1·00
3·322	1·710	1·612	1·06

The first column gives the concentrations of the potassium iodide in millimols per litre, and this is also the sum of $I' + I_3'$; the second is the amount of iodine dissolved after subtraction of the constant amount of 1·342, the solubility of iodine in pure water; it gives the concentration of the tri-iodide ion I_3'; in the third column are the concentrations of the unchanged iodide ion I', obtained by subtraction of the second from the first column. The last column contains the ratio I'_3/I', which, according to the theory, ought to be constant. The agreement is quite satisfactory; about half the iodide ion unites with iodine to form tri-iodine ion, or the dilute potassium iodide solution dissolves as much iodine as the combined iodine contained in it.

When the solutions are very concentrated much more iodine is dissolved than the proportional amount. Accordingly, a saturated solution of iodine in concentrated potassium iodide deposits solid iodine when it is diluted with water. The cause probably lies in an alteration of the solvent; owing to its greater chemical similarity, the concentrated solution of potassium iodide is a better solvent than the dilute solution.

If two of the substances are in the solid state in contact with the solution, the system is comparable with that of two solids and a vapour. The equilibrium, which is represented in the solution by $a_1^{m_1}a_2^{m_2} = kb^n$, is simplified because two of the three concentrations are constant. The third is also constant, and there is a fixed composition of the solution, which varies only with the temperature, but is absolutely independent of the amounts of the solids and of the initial composition of the solution.

The double salts are examples of this case. While, for example, the solubility of copper sulphate in a solution, which contains potassium sulphate, alters with the concentration of the latter, so that it has been called the "displacement" of the one salt by the other, the concentration becomes independent of the amount of potassium sulphate, as soon as the double salt potassium copper sulphate occurs as a solid along with the solid copper sulphate. If equilibrium has not yet been established, solution or separation of the salts of one or both takes place, until the fixed concentrations of all the components have been reached.

Evidently there are in this case three equilibria, according as the two components, or one or other of them and the compound, are present as the solid phases. In the present instance, they are solution with potassium sulphate and copper sulphate, solution with potassium sulphate and double salt, solution with copper sulphate and double salt. One of the three equilibria is in general unstable; in the present example it is the first, and a solution saturated with both components will spontaneously deposit the double salt after some time, one of the single salts disappearing during this process; in this way the new equilibrium is established.

Such cases of equilibrium are not adapted for testing the law of mass-action, as the ionisation introduces a complication which is very difficult to overcome.

An example which illustrates the three equilibria, and is not open to the above objection, is the formation of the compound of anthracene and picric acid (containing one mol of each) in alcoholic solution (Behrend, 1894).

The following table contains the solubility results at 25°:

SOLID PHASES

	Anthracene.					Anthracene and Picrate.
	1	2	3	4	5	6
Anthracene	·176	·190	·206	·215	·228	·236
Picric acid	...	1·017	2·071	2·673	3·233	3·469
Anthracene free = a_1	...	·176	·176	·176	·176	·183
Picric acid free = a_2	...	·999	2·032	2·623	3·106	3·401
Picrate = b	...	·032	·069	·089	·119	·121
a_1a_2/b	...	5·5	5·2	5·2	4·7	5·1

	Picrate.				Picric acid and Picrate.	Picric acid.
	7	8	9	10	11	12
Anthracene	·202	·180	·162	·151	·149	...
Picric acid	3·994	5·087	5·843	6·727	7·511	7·152
Anthracene free = a_1	·140	·127	·109	·098	·096	...
Picric acid free = a_2	3·926	5·019	5·775	6·659	7·443	...
Picrate = b	·121	·121	·121	·121	·121	...
a_1a_2/b	4·8	5·3	5·2	5·4	5·2	...

The numbers are parts by weight in 100 parts of the solution. Each column gives the composition of a definite solution, which is in equilibrium with the solids under which it stands. The rows have the following meaning.

The "anthracene" and "picric acid" rows contain the direct results of analysis, giving the sum of the combined and uncombined amounts of these components. To ascertain how much the uncombined part comes to, solubility determinations of the two components in the pure state were carried out; these are given in columns 1 and 12. All the solutions in equilibrium with solid anthracene must contain ·176 of it, and the excess of anthracene above this amount is present as picrate. The same holds for solutions saturated with picric acid. In this way the free parts and the amount present as picrate in the different solutions are calculated. The amount of picrate calculated from the compositions of solution 6 and solution 11 should be the same for the two solutions, since they are both in equilibrium with solid picrate. On making the calculation we find that they are practically in agreement, though it is only moderate owing to the considerable errors of experiment.[1]

The expression a_1a_2/b is constant, as is seen from the last row, or, rather, it oscillates round a mean value. In solutions 2 to 6 a_1 is constant, whence $a_2/b = \text{constant}$; in solutions 6 to 11 b is constant, whence $a_1a_2 = \text{constant}$. In solutions 6 and 11 two solid phases are present; there is only one composition for each of them, independent of the amounts of the components present. No attempt was made to prepare the third constant solution which would be in equilibrium with anthracene and picric acid. It is in the unstable region, but it is possibly in the metastable region, in which case the solution could still be prepared, although it would be supersaturated with respect to the picrate.

The Distribution Law. — Another very interesting case of equilibrium in solution occurs when there are two liquid phases. If two liquids are practically immiscible, and a substance is added which can dissolve in each, it will be distributed between the two solvents, as a gas distributes itself between the gas space and a liquid solvent. Henry's law, that the concentrations in the two phases are in a constant ratio, is literally true in this case also. The ratio is known as the distribution coefficient.

When a gas dissolves in a liquid, the concentration in the liquid is naturally referred to that in the gas; but there is no such natural preference in the case of two liquids, and, in working with distribution coefficients, care should be taken to state which liquid is taken as standard. The statement that the distribution coefficient of succinic acid in water and ether is 6·0 means that the equation

$$\frac{\text{concentration in water}}{\text{concentration in ether}} = 6{\cdot}0$$

is satisfied.

This law was discovered by Berthelot and Jungfleisch (1872), and was proved by a number of examples. Later, numerous applications of the law, especially by W. Nernst, have demonstrated its accuracy

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[1] On this account, the amount of free anthracene is given in solution 6 as ·183 instead of ·176.

and the wide extent of its validity. The following series of observations with succinic acid will serve to illustrate it.

Concentration.		Ratio.
In Water.	In Ether.	
42·4	7·1	6·0
43·8	7·4	5·9
47·4	7·9	6·0

If the investigation is carried much further the distribution coefficient is found to change. There are two reasons for this. In the first place, the condition of a solute often alters with the dilution, chemical action with one or other solvent taking place. The effect this will have on the distribution coefficient is easily understood from the considerations given on p. 307. If the chemical action reduces the number of mols present, the relative quantity of the compound will increase with increase of concentration. On the assumption that this part remains mainly in the solution in which it is formed (and this is in most cases justified), the distribution coefficient will increase in favour of this solution when the concentration increases, and will decrease when the concentration diminishes. Conversely, if the number of mols of a substance increases owing to the chemical action of the solvent, it will, on dilution, accumulate more and more in the solution in which this increase takes place. If the number of mols remains unchanged, dilution has no influence on the distribution coefficient, although chemical actions may take place between the solvent and the solute.

In the second place, the deviations from the simple laws of solutions which occur at greater concentrations may cause an alteration of the distribution coefficient. Not only is the behaviour of the substance to the single solutions changed, but the mutual solubility of the two solvents, which is always present, however small it may be, is also changed when considerable quantities of the third substance are present. This generally takes the form of increased mutual solubility, and the distribution coefficient no longer refers to the same solvents as before.

The applications of this distribution law are numerous and extensive. In complicated cases, in which several substances are concerned, it is enlarged after the analogy of Dalton's law of the solubility of mixed gases; the distribution is then regarded as independent of the presence of other substances (which also undergo distribution). This assumption is only a limiting case, which is not justified even at comparatively small concentrations, so that one must be prepared for measurable deviations from the simple distribution law.

Conclusion.—Cases in which more than three components appear can be treated in a similar manner to reactions of the third order.

Although they are of greater complexity, no really new points arise, and a survey of the general relations can be made on the same general principles. To enter upon a detailed account of them is beyond the scope of this book.

The present treatment of equilibrium problems is essentially formal, since the form of the relations between the defining magnitudes has been taken into account, but not the connexion between the constants and the chemical nature of the substances concerned.

This is a problem which really belongs to descriptive Chemistry, and the text-books of the future will contain such data as well as melting- and boiling-points. Our present knowledge, however, of these magnitudes is so little developed that they cannot be employed as general aids to description. Some account of what is known in this direction will be given later on.

BOOK IV

ELECTROCHEMISTRY

CHAPTER XV

ELECTROLYTIC CONDUCTION

General.—A rod of perfectly pure zinc is not attacked by dilute sulphuric acid, neither is a rod of platinum. But if we immerse simultaneously a zinc rod and a platinum rod in the acid and bring the projecting ends into contact, either directly or by means of a metallic wire, the zinc is dissolved, and the hydrogen expelled from the acid appears on the platinum. The connecting wire has at the same time assumed peculiar properties; if a magnetic needle is held parallel to it, the needle suffers immediate deflection; if it be cut at any point and the ends placed apart from each other on a piece of litmus paper moistened with a solution of salt, there appears at the end connected with the zinc a blue speck, and at the end connected with the platinum a red speck; lastly, the wire becomes warm. All these phenomena cease on the removal of one of the metals from the liquid.

They serve to show that with the arrangement described, the chemical action between zinc and sulphuric acid produces effects at a distance from where it actually takes place, in the wire namely. The chemical energy produced where the acid attacks the zinc must therefore have been transformed into another form capable of passing through metals and liquids, and of exercising chemical and thermal actions at any part of its course.

The only change to be observed in the properties of the substances taking part in the action is that the metals have become charged with electricity, the charge on the zinc being negative and on the platinum positive. If the two metals be connected by a conductor the difference is not adjusted, for after the removal of the conductor the metals are again found to be charged. But we know that opposite electrical charges in metallic conductors neutralise each other. It only remains, therefore, to conclude that the charges are continually neutralised by means of the connecting wire, but that they are just as regularly reproduced in the metals. By this process there comes into existence in the system what is termed an electric current.

The electric current is connected with the chemical action on the zinc, not only in point of time, but also causally. The current ceases when the chemical process is in any way prevented: it can perform work, and consequently contains energy, which it must derive from the chemical process, this being the only available source. We may thus say that, in the system we have described, chemical energy is transformed into electrical energy.

Conservation of Energy.—The transformation must, in the first instance, be subject to the law of the equivalence of energy. Since, during the solution of zinc in sulphuric acid as usually performed, all the chemical energy is transformed into heat, so much less heat must appear at the seat of reaction, the more electrical energy passes into the connecting wire. If this also is changed into heat, the sum of all the different quantities of heat produced must be constant, and equal to the heat of solution of the zinc.

These consequences of the fundamental principle of energy have been experimentally tested by Joule and especially by Favre (1854), and confirmed in all particulars. From a system consisting of zinc, sulphuric acid, and platinum—a voltaic (or galvanic) element as it is usually called—more than half the heat of solution of the zinc may be obtained in the form of electrical energy; but if this be again changed into heat by conducting the current through a long thin wire, the original quantity of heat is exactly reproduced.

By making use of the electromagnetic forces we can transform the electrical energy, obtained from the chemical, into work. The total evolution of heat in this case is smaller by the thermal equivalent of the mechanical work done. This result was also confirmed by Favre.

Lastly, we can use the electrical energy to perform chemical work. If the current from several such voltaic elements is conducted to two platinum plates immersed in dilute sulphuric acid, a development of oxygen and hydrogen takes place on these. The total heat given out is again less than before, and that exactly by the amount of the heat of combination of the two gases to form water. Here once more we have strict fulfilment of the law of the conservation of energy.

The Factors of Electrical Energy.—Like the other forms of energy, electrical energy appears as the product of two factors, one of which is called the quantity of electricity, the other—potential, tension, or electromotive-force. The first factor is a capacity, the second an intensity, so that electrical energy capable of unrestrained movement in a system can only assume a permanent stable state when the second magnitude is the same throughout the system. When this is not the case, a change of state occurs from which work may be obtained, just as it can be got from a change of state of heat or of any other form of energy.

The other factor, the quantity of electricity, is usually looked upon as being the real existent thing that lies at the bottom of all electrical phenomena, and the whole nomenclature of electrical science has been formed in accordance with this conception. Although the view has often been found very convenient, it must still be borne in mind that the thing underlying electrical phenomena is electrical energy, and that the nomenclature usually adopted is only of value as affording us, in many cases, a means of clear and concise formulation.

The Electric Current.—If the quantity of electricity in a voltaic current passing through a section of the conductor in one second be denoted by i, current strength; and the electromotive-force between two parts of the circuit by E; then, by definition, the energy corresponding to this motion of electricity is Ei. If the current in the part of the circuit considered performs no external work, its energy is completely transformed into heat; if we denote this by W, we get

$$W = Ei.$$

We are accustomed to conceive the way in which electrical energy passes into heat as being analogous to the conversion of the mechanical work of a flowing liquid into heat—a sort of friction is supposed to resist the motion of the electricity, and the operation of overcoming this conditions the transformation of the electrical energy into heat. The electromotive-force corresponds to the pressure under which the liquid moves. We therefore define the resistance R of a conductor in accordance with these ideas, as the quotient of the electromotive-force E, by the quantity of electricity forced by it through the conductor in unit time, *i.e.* by the current strength i. R is found to be independent of the electromotive force and the current strength. We have thus

$$R = \frac{E}{i} \text{ or } i = \frac{E}{R}.$$

This is the well-known law of Ohm, that the current strength is equal to the electromotive-force divided by the resistance.

Experience has proved it to be a general law of nature, which is independent of any particular representation of the nature of electrical resistance.

If in the equation W = Ei we substitute for E the equivalent value Ri it follows that

$$W = Ri^2.$$

The quantity of heat developed by the passage of electricity through a conductor is proportional to the square of the current strength (the quantity of electricity passing per second) if the resistance is constant, and proportional to the resistance if the current strength is constant. This law was experimentally discovered by Joule (1841) and has frequently received confirmation.

Units.—For the magnitudes above defined units have been introduced, which, in a manner that cannot be explained here, have been derived from the consideration of electrostatic and electromagnetic processes. As unit of resistance we take that at 0° of a column of mercury 106·23 cm. long, and 1 sq. mm. in section; this resistance is called an ohm. The unit of current strength is so defined that 0·001118 g. of silver is separated in one second; this is called an ampere, and the quantity of electricity transported in a second is a coulomb. The tension[1] which is required to cause unit of current to flow through a conductor of 1 ohm resistance is taken as unit of tension, and is a volt. A voltaic cell of cadmium and mercury in the saturated solution of their sulphates has the tension 1·0186 volt. This unit is specified by the equation

$$i = E/R,$$

and the values of R and i defined above.

These magnitudes are so chosen that the electrical energy, volt × coulomb, is equal to 10^7 absolute units or ergs. It has already been mentioned under the name Joule as a general practical unit of energy. From the data given on p. 249, we obtain as a value of the Joule that a current of 1 volt tension passing for 1 second through a resistance of 1 ohm, 1 coulomb being thereby set in motion, develops sufficient heat to raise 1 g. of water from 0° to 0·239° C.

Faraday's Law.—The motion of electricity in bodies which admit of it at all takes place in two distinct ways. When electricity passes through conductors of the first class, these only experience heating according to Joule's law (see above), and no other material change. Metals, alloys, carbon, and a few other substances constitute this class.

Conductors of the second class can only permit the movement of electricity in such a way that a chemical change takes place in them simultaneously. The chief members of this class are salts, fused or in solution, and further, aqueous solutions of acids and bases—all of these being compound substances, as we see.

In such conductors of the second class, or electrolytes, the movement of electricity takes place so that the metals (or metallic radicals) of the salts and bases, and the hydrogen of the acids, move from the positive part of the circuit to the negative, while the acid

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[1] For the sake of brevity, "tension" is used instead of the longer "potential difference" or "electromotive force."

radicals or elements, such as chlorine, bromine, iodine, and also the hydroxyl of bases, move in the opposite direction. These components, the ions, are set free where the electrolyte is in contact with metal conducting the current.

Faraday in 1833 discovered the general law that equal quantities of electricity on passing through different electrolytes require equivalent quantities of the ions for their transport. If several different electrolytes are introduced into the same circuit (in which according to the laws of electricity equal quantities of electricity pass through every section in equal times), then the quantities of the liberated metals or hydrogen, as well as those of the acid radicals, are in equivalent proportions.

We know that the equivalent of an element is its atomic weight divided by its valency. If we have, for example, solutions of silver nitrate, cupric sulphate, and antimony trichloride in a series in the same circuit, the quantities of metal simultaneously deposited are in the proportion of 108 of silver to $\frac{1}{2}$ 63·3 of copper to $\frac{1}{3}$ 120 of antimony. Of the acid radicals we obtain at the same time, NO_3, $\frac{1}{2}$ SO_4, and $\frac{1}{3}$ Cl_3.

The electrolytic submolecules of equal valency behave as if each had the same capacity for electricity, so that equal quantities of electricity are conveyed by the same number of them, no matter what their nature. Recent researches have led to the view that electric energy only occurs in definite, very small, independent quantities of electricity, to which the name electron is applied. Each ion is in combination with as many electrons as it has valencies.

We know that there are certain substances, especially metals, which can act with different valencies; thus, for example, mercury and copper are univalent and bivalent, tin bivalent and quadrivalent, iron bivalent and trivalent. According as one or other set of these compounds is used for conducting the current, each atom transports so many times the electricity capable of being transported by a univalent atom as the metal has active valencies in the compound in question, or is united with a corresponding number of electrons.

If we take the electricity transported by one gram of hydrogen as our unit, 63·3 g. of copper in cuprous compounds convey one unit, and the same quantity in cupric compounds two units. In a similar way, 56 g. of iron in ferrous compounds transport two units, and in ferric compounds three units. The group $Fe(CN)_6$ as a component of potassium ferrocyanide transports four units of (negative) electricity; but in potassium ferricyanide only three. Having regard to this property we shall continually distinguish between univalent, bivalent, trivalent, etc., ions. Hydrogen and the metals, which convey positive electricity, are called positive ions or kations; the halogens and other acid radicals, by means of which the negative electricity is transported, are called negative ions or anions.

In order to understand Faraday's law we must carefully guard against the error of supposing the separation of the ions at the electrodes, *i.e.* the places where the electricity passes from the electrolyte into the metallic portion of the circuit, to be the essential part of the law. That is not the case; the law refers rather to every kind of motion of the electricity within conductors of the second class. Of course the separation of the ions at the electrodes is the only means of proving the accuracy of Faraday's law, and as far as this proof has yet been taken the law holds strictly true; the quantity of electricity is always exactly proportional to the amount of the ions separated, and the latter are always in the ratio of their equivalents for equal quantities of electricity. In particular, not the slightest indication has been obtained of metallic conduction, which some physicists think possible, *i.e.* conduction of electricity independent of motion of the ions.

Application to the Voltaic Cell.—As Faraday's law holds good for all movements of electricity within electrolytes, the development of electricity in voltaic elements (p. 378) must also be determined by it. If the ions of sulphuric acid in the system [zinc, dilute sulphuric acid, platinum] move so that the group SO_4 goes towards the zinc and forms zinc sulphate with it, while H_2 moves towards the platinum and is evolved there as gas, then two units of electricity as above defined must be set in motion for every 65·4 g. of zinc dissolved, or 98 g. of sulphuric acid decomposed. We may say in general that every voltaic element, independent of its nature or of the character of the chemical process, produces the same quantity of electricity by consuming one equivalent of the metal.

It is of interest for many purposes to know the quantity of electricity moving with 1·0078 g. of hydrogen or with the equivalent quantity of another ion. According to the experiments of Kohlrausch and Lord Rayleigh this amount is 96,540 coulombs, this being represented by the symbol F. Conversely, a coulomb requires for its transport in an electrolyte ·00001036 gram-equivalents of any ion.

This consequence from Faraday's law, that every voltaic element on the consumption of one gram-equivalent of its active substances always sets 96,540 coulombs in motion was extensively confirmed by Renault (1867). There were found to be numerous examples of a metal having different electrochemical equivalents, always in rational proportions, according to the nature of the compounds containing it. Thus 96,540 coul. are set in motion by 200 g. of mercury dissolving in dilute nitric acid to form mercurous nitrate, but 100 g. are sufficient when the solvent is potassium cyanide, mercuric cyanide $Hg(CN)_2$ being formed. The electrochemical equivalent of copper in dilute hydrochloric acid is 63·3, cuprous chloride being the product, while in dilute nitric acid it is 31·7, for then cupric nitrate is formed. Tin usually acts with the equivalent

$\frac{1}{2}$ 118; but in potassium pentasulphide, when it dissolves with formation of SnS_2, its equivalent is only $\frac{1}{4}$ 118. Tellurium in hydrochloric acid has the equivalent $\frac{1}{2}$ 126·5, in potash $\frac{1}{4}$ 126·5.

Faraday's law both in this form and in that respecting electrolysis was formerly misunderstood as meaning that equal quantities of electricity in the various equivalents conditioned the same expenditure or gain of work; Berzelius in particular was a violent opponent of the law owing to this misunderstanding. From our point of view we see that there is no question of energy or work here at all. Faraday's law only considers one factor of electrical energy, viz. quantity; the other factor, electromotive-force, remains unheeded.

Electrolytic Conduction.—We have already learned that by no means all compound substances are capable of conducting electricity electrolytically, *i.e.* by help of ponderable particles. The property is possessed principally by aqueous solutions of salts, acids, and bases; it is only observed with those substances that can instantaneously effect an exchange of their components.

If we think for a moment that, according to Faraday's law, for the purpose of electrolytic conduction particles laden with positive electricity must move in one direction, while particles charged with negative electricity move in the other, we see that the ability to conduct depends on the ability to form such vehicles for the electricity. Now electrical energy is a binary form of energy, and polar in nature; positive or negative electricity cannot exist alone, but both result simultaneously and in such quantities that their algebraic sum is zero. A substance which can effect electrolytic conduction must split up into two equivalent parts, which carry equivalent amounts of positive and negative electricity. These are called the ions of the original, non-electric, and non-conducting substance; those which travel in the direction of the positive current are kations, the others are the anions.

Formerly, therefore, electricity had ascribed to it the property of effecting this decomposition on its entrance into an electrolyte, and of availing itself of the fragments for its own transport. Several facts, however, are at variance with this view. A certain amount of work would evidently be required to effect such a decomposition, but electricity according to our experience moves in electrolytic conductors with the same freedom as in metals; there is consequently no place for such work. Clausius therefore (1857) assumed, in unconscious agreement with an idea developed by Williamson (1851) for quite other purposes, that a small fraction of the molecules in electrolytes are decomposed into their components; the parts, already separated, are immediately seized on by the electricity to effect its transport, so that it has to perform no work in the matter at all.

The question soon arises as to the proportion of decomposed molecules in a definite electrolyte, *e.g.* in a normal solution of potassium chloride (74·5 g. per litre). Clausius left this question unanswered and only stated his general opinion that the number was not necessarily large. The influence of dilution on electrolytic conductivity led Arrhenius (1887) to the opposite view, that in ordinary dilute solutions the number is very considerable. The general laws of electric conductivity, on which this conclusion is based, will now be dealt with in some detail.

Conductivity.—If a conductor of either kind be introduced into a circuit, the resistance, according to Ohm's law, is independent of the current strength, but it depends upon the temperature, the form, and the chemical nature of the conductor. As to form, the resistance is proportional to the length and inversely as the cross-section of the conductor; it is eliminated by referring the resistance to a cylinder or prism of 1 sq. cm. cross-section and 1 cm. in length (*e.g.* a cube with 1 cm. side). This resistance in ohms is the specific resistance of the substance at the given temperature.

The resistance of electrolytic conductors, *e.g.* of salt solutions, is approximately inversely proportional to the concentration of the solution; the conduction depends upon the amount of salt present. It is therefore better to substitute for resistance its reciprocal conductivity, $L = 1/W$, which varies directly with the concentration.

Conductivity varies, however, with the amount of salt. As equal quantities of electricity are conveyed by chemical equivalents of substances (Faraday's law) it is convenient to refer conductivity to electrically or chemically equivalent quantities of the salts present in solution. The corresponding definitions can be obtained as follows:

Imagine a vessel formed of two electrodes of great extent, 1 cm. distant from each other, and the necessary non-conducting walls. Let so much of the electrolytic liquid be introduced into this vessel that it contains a gram-equivalent of the electrolyte. This system will have a definite resistance in ohms and a corresponding conductivity; this is the equivalent conductivity.

If the vessel contained a mol of the substance instead of an equivalent, the conductivity would be the molar or molecular conductivity. For univalent electrolytes the two are the same; for multivalent ones, the molar is a multiple of the equivalent conductivity. The equivalent conductivity of a given electrolyte depends in the first instance on the temperature, increasing almost without exception with rise of temperature, and mostly by about 2 per cent per degree. It is further dependent on the state of dilution, increasing almost always simultaneously with this. The increase is very considerable for bad conductors, small for good conductors, the molar conductivity everywhere approximating with increase of dilution to a limiting value which can be practically attained by good conductors; in the case of bad conductors, such as acetic acid or ammonia, even at the most extreme dilutions accessible to measurement, the molar conductivity is still far removed from the limit.

Methods.—The measurement of the electric conductivity of electrolytes was for a long time a very difficult operation; a method at once convenient and exact was first given by Kohlrausch (1880). Such measurements are almost inseparably bound to the use of electrodes which, as soon as the current passes from them into the electrolytic liquid, become through "polarisation" the seat of unknown electromotive-forces (*vide infra*), so that the usual methods for conductors of the first class are not applicable here at all. By substituting alternating currents (*i.e.* currents that incessantly change their direction) for ordinary currents, Kohlrausch succeeded in obviating the disturbing influence of polarisation, and in rendering exact measurement possible.

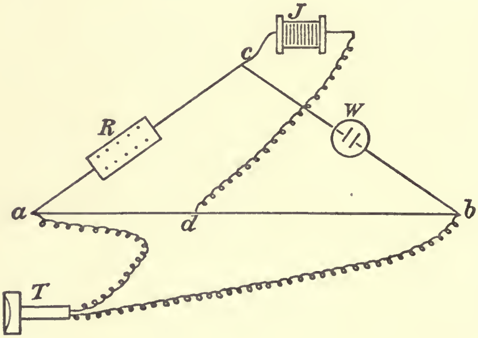

Fig. 56.

His apparatus is constructed on the plan of Wheatstone's bridge, and is diagrammatically represented in Fig. 56. The alternating currents of a small induction coil J are conducted by means of a sliding contact d to a wire[1] 1 metre long and stretched on a scale divided into millimetres. On the one hand, they pass through the wire da and db, and on the other through the resistance box R, and the conducting liquid W by the paths cRa and cWb; the telephone T is joined to a and b.

It is well known that in such an arrangement no current flows through the "bridge" aTb when the resistance R is to the resistance W as ad : db. The silence of the telephone indicates when this occurs. We therefore move the carriage with d along the wire ab until we find the spot at which the telephone no longer speaks. As $R : W = ad : db$, the resistance W required is equal to $R\frac{db}{ad}$, or the conductivity $L = \frac{1}{W} = \frac{ad}{R \, . \, db}$.

To calculate the equivalent or molar conductivity from the conductivity so obtained for the liquid in W, we must multiply the latter by the "capacity" of the resistance-cell, and also by the

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[1] The wire may be of platinum or of constantan or similar resistance wire; it should have as great a resistance as possible.

dilution, *i.e.* the number of litres in which a gram equivalent or a mol of the electrolyte is contained. The capacity is found by introducing into the cell a liquid of known conductivity and composition, and finding its resistance. If M is the molar conductivity of the liquid, and V its dilution, then we obtain the factor K for transforming the conductivity measured in the cell into molar conductivity from the equation

$$M = K . \frac{V . ad}{R . db} \text{ or } K = \frac{M . R . db}{V . ad}.$$

If we now measure another liquid of the dilution v, its molar conductivity will be

$$\mu = K\frac{v . ad}{R . db}.$$

The cells used for measuring conductivities are of different construction according to the magnitude of the conductivity, for it is found that resistances below 10 or above 10,000 ohms cannot well be measured with the apparatus. For liquids that are good conductors we therefore choose cells in which the electrodes are a considerable distance apart, and the column of liquid between them of small section; for bad conductors the conditions must be reversed. The accompanying diagrams (Figs. 57, 58) show two forms that suffice in almost all cases. The electrodes are made of platinum, and should be coated with platinum black by electrolysing a very dilute solution of platinum chloride between them, with occasional change of direction of the current, until their surface is covered with a black velvety coating.[1]

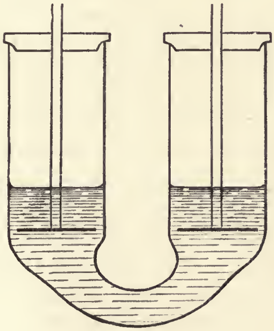

FIG. 57.

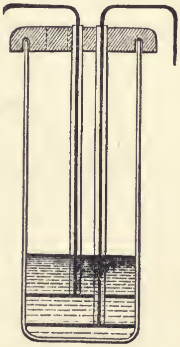

FIG. 58.

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[1] A suitable solution has the composition: water 30, platinic chloride 1, lead acetate 0·008 (Lummer and Kurlbaum); the surface is so effective that electrodes of 1 sq. cm. area can be used.

Salt Solutions.—The conductivity of equivalent (not molar) quantities of the neutral salts is of much the same order of magnitude, varying between 50 and 120, in the above units (p. 387). It increases slowly with dilution and usually reaches a maximum at dilutions of about 2000 litres. The following table, containing values observed by Kohlrausch, shows this in detail; the temperature of observation was 18°.

Dilution.	KCl.	NaCl.	LiCl.	$\frac{1}{2}BaCl_2$.	$\frac{1}{2}K_2SO_4$	$\frac{1}{2}MgSO_4$.
1 l.	98·2	74·4	63·4	70·1	71·6	28·9
10 l.	111·9	92·0	82·4	90·8	94·9	49·7
100 l.	122·5	102·0	92·1	106·7	115·8	76·2
1000 l.	127·3	106·5	96·5	115·6	126·9	99·9
2000 l.	128·1	107·2	97·2	117·0	128·6	104·2
5000 l.	128·8	107·8	97·9	...	130·1	108·1
10000 l.	129·1	108·1	98·1	...	130·8	109·9

This table presents us at the same time with another regularity. The increase of conductivity with increasing dilution is different according to the nature of the salts. The conductivity of salts with two univalent ions changes least, the change is greater for salts with one bivalent and two univalent ions, and greatest of all for magnesium sulphate, which contains two bivalent ions. This rule, that the increase on dilution is greater the greater the product of the valencies of the ions, has been proved to hold very generally.

Kohlrausch's Law.—The principle of greatest generality regulating the conductivity of neutral salts is not, however, to be seen in the preceding small table. It was discovered by Kohlrausch in 1876 and may be expressed most shortly as follows:—The conductivities of the neutral salts in dilute solution are additively composed of two values, one depending only on the metal or kation, the other only on the acid or anion.

The form of this law agrees exactly with the law of thermoneutrality and the laws for the volume and most of the other properties of salt-solutions. The reason is the same as before; the mutual independence of the conductivity of the two ions, as stated in the law, proves the corresponding mutual independence of the ions themselves.

If we attempt to represent to ourselves what goes on in the interior of an electrolyte when a current is passing, we arrive at something like the following view. The electrical motive-power which, in consequence of the difference of potential always present in the circuit, acts on the positive ions in the direction of the positive current and on the negative ions in the reverse direction, serves to set these ions in motion so that they transport electricity in corresponding paths. The conductivity (in other words, the quantity of electricity conveyed in unit time in virtue of unit electromotive-force) evidently depends on the number of the moving ions and on the speed at which they move. We must remember, too, that according to Faraday's law equivalent ions, no matter what their composition, transport the same quantity of electricity. If, therefore, we perform our calculations for equivalent quantities of the different electrolytes, as was done in the definition of the equivalent conductivity, these quantities will transport equal quantities of electricity, and the equivalent conductivity is thus a direct measure of the velocity of migration of the ions.

Here, to be sure, we make the assumption that all the electrolyte contained in solution takes part in carrying the electricity—an assumption not always justified. With dilute salt-solutions, however, this is so nearly the case that we may neglect any deviations from it, meanwhile at least.

From the difference in the conductivity of dilute salt-solutions we perceive that the velocities of migration of the ions must be different. The fact that the conductivity of potassium chloride, bromide, etc., exceeds that of sodium chloride, bromide, etc., by about 21 units shows that the potassium ion must migrate so many units faster than the sodium ion. In the same way we can ascertain the differences between the velocities of other ions; the velocities themselves, however, cannot be determined from the conductivity.

Hittorf's Theory.—We come here upon a phenomenon first rightly understood by W. Hittorf (1853). If during electrolysis the two ions (as had always been tacitly assumed) migrate at the same rate, then the loss experienced by the liquid must be equally large at the two electrodes, and the concentration round these must be equally diminished. This is in general not the case; the concentrations change unequally at the two electrodes, and from this Hittorf concluded that the two ions migrate at different rates.

In order to make the action of the different rates of migration clear let us consider Fig. 59. The black points represent the one ion, the white circles the other. During electrolysis the black points move to the left, the white to the right, the latter moving twice as fast as the former. The top row represents the condition before electrolysis, the lower row the condition after electrolysis. The vertical line xy divides the original system into two equal parts.

At the beginning of the electrolysis there are on each side eight black and eight white ions. At the conclusion, after six equivalents have been decomposed, there are four undecomposed on the left hand and six on the right hand: the concentration has become different on the two sides. On the left side, four equivalents of salt have disappeared, and two equivalents on the right. These decrements are proportional to the rates of migration of the ions. Accordingly, if we determine, after electrolysis, the decrease in the concentration of the salt at the corresponding electrodes, the ratio is equal to the ratio of the velocities of migration.

It is now easy to ascertain the share of the different ions in the conductivity. On the electrolysis of a solution of potassium chloride, for example, the concentrations at the two electrodes remain almost exactly equal; consequently the ions K and Cl move at the same rate, viz. (if we use the units of p. 387) 63·6 in solutions of 1000 l. dilution. From this it follows at once that the rate of migration of sodium is 42·2, of lithium only 29·8, etc.

By determining a single ratio of transport, *e.g.* that of potassium chloride, we can calculate the velocities of all the ions, provided the conductivities are known; and, if we know the latter, we can at once proceed backwards to the transport ratios of all the salts formed of these ions. Kohlrausch has shown that the results of such a calculation agree most completely with the direct determinations of the transport ratios made by Hittorf.

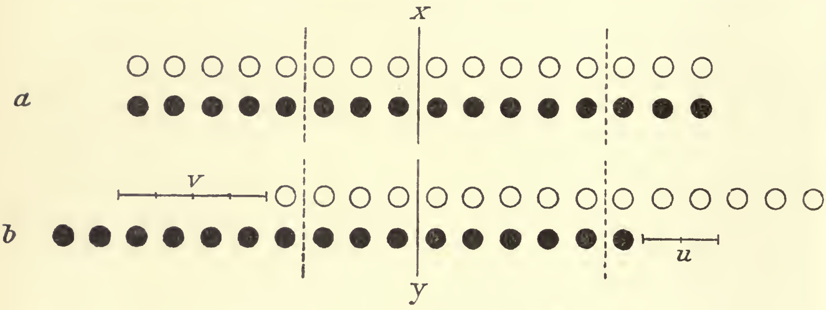

FIG. 59.

The strong acids of the type of hydrochloric and nitric acids behave similarly to the neutral salts, their conductivity, however, being much greater. As the velocity of the negative ions is known, the greater conductivity can only be due to the great velocity of the hydrion. The following table contains the equivalent conductivities at 18° of a few acids measured by Kohlrausch:—

Dilution.	HCl.	HNO_3.	$\frac{1}{2}H_2SO_4$.	$\frac{1}{3}H_3PO_4$.	$C_2H_4O_2$.
1 l.	301	310	198	22	1·32
10 l.	351	350	225	...	4·60
100 l.	370	368	308	85	14·3
1000 l.	375	373	355	106	41

At a dilution of 1000 l., when chloride ion has a velocity of 63·3, we get for the hydrion of hydrochloric acid, and consequently for hydrion in general, a velocity of 311. Hydrion therefore migrates five times as fast as chloride ion.

Great changes of concentration must thus appear at the electrodes when acids are electrolysed. These changes have also been measured by Hittorf, and Kohlrausch has shown that they are in perfect concordance with the theory of the independent migration of the ions.

Kohlrausch gives the conductivity of bases at 18° as follows :

Dilution.	KOH.	NaOH.	NH_4OH.
1 l.	184	160	·89
10 l.	213	183	3·3
100 l.	228	200	9·6
1000 l.	234	208	28·0

From the velocity of migration of potassium ion, which is 64·4, it follows that the velocity of hydroxidion OH′ is 172, which, therefore, migrates considerably faster than the other negative ions, *e.g.* about 2·5 times as fast as chloride ion—one of the next fastest.

Electrolytic Dissociation.—While the strong acids and bases thus obey the law of Kohlrausch, the weak acids and bases diverge from it exceedingly. Neither phosphoric acid, nor acetic acid, nor ammonia gives numbers that can be brought into harmony with the law, for their conductivities are smaller than the velocity of migration of hydrion on the one hand, and hydroxidion on the other, so that even the assumption that one of the ions did not move at all would still give much larger numbers than those observed.

The explanation of these abnormalities may be found in the fact that we have neglected in our last considerations a factor of the conductivity which has been already indicated. The equivalent conductivity can only be represented as the sum of the velocities of migration of the ions, when the number of ions conveying electricity is the same in all cases. Now it is true that we have compared solutions containing equivalent quantities of the different electrolytes, but we have still to find out whether equal numbers of free ions are contained in these equivalent quantities, for the ions alone are active in the conduction of electricity.

Determinations of the freezing-point of solutions show that hydrochloric acid and potash exert an influence almost twice as great as that which corresponds to their molar weight—they are thus almost completely dissociated into their ions. Acetic acid and ammonia, on the other hand, depress the freezing-point almost as indifferent substances, *i.e.* as calculated from their molar weight—very few free ions exist in them. Phosphoric acid lies between the two, but nearer acetic acid than hydrochloric acid ; it is thus partially, but still very far from fully, dissociated into its ions.

Consequently the law of Kohlrausch is not to be written in the form $\mu = u + v$, where μ is the molar conductivity and u and v the velocities of migration of the ions, but in the form

$$\mu = x(u + v),$$

x representing the portion of the electrolyte dissociated into its ions.

Only at infinite dilution does the dissociation become complete, when the corresponding conductivity μ_∞, x being 1, is given by the equation

$$\mu_\infty = u + v.$$

The law of Kohlrausch, therefore, only holds strictly for infinitely dilute solutions.

It has been already mentioned that the salts, especially those with univalent ions, are as good as completely dissociated at dilutions practically attainable (at about 1000 l.); further dilution does not alter their condition. The same applies to strong acids and bases. For these substances, therefore, we can determine μ_∞ with sufficient approximation. The salts of weak acids with strong bases and of weak bases with strong acids behave similarly to salts with both components strong. Consequently, by investigating such salts we can ascertain the velocity of migration of the ions of weak acids and bases, so that this property is accessible to measurement for all ions whatsoever.

If we are thus in possession of this knowledge of the values of u and v for every electrolyte, we can easily calculate the portion x of the electrolyte dissociated into ions, or the degree of electrolytic dissociation, from the equations

$$\mu = x(u + v)$$

$$\mu_\infty = u + v;$$

for by division we obtain

$$x = \frac{\mu}{\mu_\infty}.$$

The degree of dissociation of a dissolved electrolyte at any state of dilution is equal to the ratio of the molar conductivity at this dilution to the molar conductivity at infinite dilution.

Independent Evidence of Dissociation. — A new question here arises. The above considerations rest exclusively on an electrical basis; the phenomena of electrolytic conduction led to the view that the substances which act as carriers of electricity in electrolytes are in a special state of dissociation, which depends upon the dilution, the temperature, and the nature of the substance. The extent of this dissociation conditioned the amount of conductivity, the other conditions being comparable; and, conversely, measurement of the conductivity gives the extent of the dissociation.

We have already been led to a similar conclusion by the deviations of certain dissolved substances from the simple laws of solutions. If these considerations are right, electrolytic conductivity and divergence from the laws of solutions should go hand in hand; further, both should occur only in the same substances, and to the same relative extent. This conclusion is fully borne out by the facts. In every case, a substance which in solution deviates from the laws of solutions, so that its osmotic pressure (or the change of freezing-point or boiling-point) is greater than corresponds to its molar weight, shows also electrolytic conduction, and *vice versa*. This relation holds quantitatively as well as qualitatively: the degree of dissociation into ions is given both by the osmotic methods and by the electrical conductivity.

Thus, on the one hand, the osmotic methods, as well as the stoichiometrical and chemical phenomena, and, on the other, the electrolytic phenomena lead us to the same representation of the condition of dissolved salts, and all these subjects are brought into intimate connexion. So much is this so, that we can frequently deduce the hitherto unknown behaviour of a substance in one of these respects from its known behaviour in the other. Such deductions have been frequently made, and have been fully confirmed by experience.

CHAPTER XVI

IONS

Salts.—Since the most widely differing phenomena presented by salt-solutions lead us to the conclusion that in them a part of the salt is decomposed into two coexistent but independent components, to which the name ion has been given, it is now desirable to give some account of their nature, more especially as in many respects their properties differ markedly from those of other substances.

The first question, "What substances can form ions?" is easily answered: salts (Hittorf, 1853). Under this name we understand a group of binary compounds which are characterised by the readiness to enter into chemical reactions, and the rapidity with which the reactions take place. These reactions do not take place between one or other elements of the salts but between the particular dissociation products, the ions.

In the great class of inorganic salts there is no doubt as to this characteristic, but it is uncertain whether some organic substances are to be reckoned as salts or not. In particular, one is inclined to class the esters, the compounds formed from acids and alcohols with loss of water, just as salts are formed from acids and bases, as salts. The criterion of the extremely great velocity of reaction shows this not to be justified; esters do not change their components instantaneously, but more or less slowly, sometimes not even to a measurable extent. Esters, therefore, are not to be considered as salts, in spite of the formal analogy of their formation.

Another criterion of salts is in accordance with this conclusion. If electrolytic conductivity depends upon the presence of ions, and their formation is characteristic of salts, the esters, if they are not salts, should be non-conductors. This is the case; esters, alone or in solution, do not conduct electricity to any considerable extent.

Still, there is a very slight conductivity, and also a slow interaction. We must therefore conclude that esters do possess the essential property of salts, *i.e.* dissociation into ions, although only in a feeble degree. And in fact this is the truest expression of experience. The limitation of salts as a class is not sharply defined, but depends in part upon our means of observation and measurement. This is a peculiarity which appears at every attempt at classification of a multiplicity of phenomena. The principal type, in which the characteristic property is most strongly developed, is easily recognised and placed, while in other cases it is less pronounced, and no sharp limit exists. We may therefore call all those substances salts in the widest sense, which we can prove to give rise to ions, *i.e.* in which we can observe reciprocal change of corresponding dissociation products, and electrolytic conduction.

Electrical Properties of Ions.—The connexion between ion-formation and electric conductivity points to the electric phenomena as being the essential feature in ion-formation. Salts decompose into components which act as carriers of positive and negative electricity. These components are therefore to be represented as united in some manner with these quantities of electricity. It does not matter whether the representation be molecular, in which the ions are looked upon as small electrically charged particles; it is sufficient to say that the formation of ions, and the formation of proportional quantities of positive and negative electricity are inseparably bound together.

An immediate consequence of this is that only equivalent quantities of positive and of negative ions can be produced at any one time, for it is a fundamental principle of electricity that only equal amounts of the opposite kinds of electricity can be produced from a body which is originally electrically neutral. This equivalence of the oppositely charged ions is an essential condition in all possible reactions, since all reacting solutions fulfil this condition at the outset.

If the two oppositely charged ions are present in equal amount in an electrically neutral solution, an electrically charged electrolyte will contain an excess of the corresponding ion. This was established by Ostwald and Nernst (1890). But the quantity of electricity which can be accumulated in a given electrolytic solution by an electrostatic charge is exceedingly small in comparison with the quantity of electricity associated with the ion in accordance with Faraday's law (p. 383), so that a very considerable charge corresponds to so small a quantity of substance that special means are required to make the effect recognisable.

Composition of Ions.—The chemical constitution of ions is easily made out in the case of the simplest salts. The ions of potassium chloride can only be chlorine and potassium (or their hydrates). Accordingly, all components of salts which can replace potassium are kations, and all which can replace chlorine are anions. While kations are generally elementary in nature and formed from metals, the number of elementary anions is relatively small; they are the halogens and the elements of the sulphur group.

Compound kations are ammonium NH_4 and its derivatives, and the analogous compounds of the other elements of the nitrogen group. Other multivalent elements can form similar organic kations, as *e.g.* sulphur in the sulphines, and many metals in their alkyl derivatives.

Compound anions are very numerous; most of them contain oxygen. Their composition is that of the corresponding acid minus hydrogen.

Valency of Ions.—While Faraday's law affords no direct means of ascertaining whether an ion is univalent or multivalent, this can frequently be done from the chemical formula, and with certainty from the osmotic laws.

In dilute solution of potassium chloride, for instance, the molar depression of the freezing-point is double the normal value; from this it is to be assumed that one mol of undissociated potassium chloride has split up into two mols of ions. For barium chloride the ratio is 1:3, corresponding to the formula $BaCl_2$; barium ion must be considered as bivalent, one mol being equivalent to two mols of chloride ion. If the combining weight of barium was reduced to half in order to write barium ion univalent, the salt baCl (ba represents barium with the combining weight 68·7) would give twice the normal depression, the quantity represented by $BaCl_2$, four times the normal depression. Since experiment shows the depression to be three times the normal value, the ion is bivalent and Ba = 137·4. The same laws hold for ions as for the molar weights of ordinary compounds, and there are bivalent and multivalent ions as well as univalent ions.

Univalent kations are formed by the alkali metals, by silver and thallium among the heavy metals, also by copper in cuprous compounds. Mercury in mercurous compounds forms both univalent ions and, at greater concentrations, bivalent ions of the formula Hg_2, which differ in many respects from the univalent simple ions. Univalent ions are also formed by ammonium and its numerous derivatives.

Bivalent kations are produced from the metals of the alkaline earths, and of the iron and copper groups; bivalent tin ions are present in stannous salts. The compound bivalent kation uranyl, UO_2, is worthy of notice.

Trivalent kations are formed from the earthy metals and their analogues, as chromium, and iron (in the ferric salts); quadrivalent ions from the metals of the tin group. In these, however, the tendency to form kations is very slight, in agreement with the feeble basic properties of the corresponding oxides. Kations of higher valency are scarcely known; zirconium and thorium ions are quadrivalent.

Each mol of these multivalent ions carries with it two, three, or four times the quantity of electricity $F = 96540$ coul. (p. 383) that univalent ions do according to Faraday's law.

There are likewise multivalent anions, in addition to the univalent ions. The latter are formed by the halogens, fluorine, chlorine, bromine, iodine, and the similar (compound) cyanogen, thiocyanogen; further, all the anions of other monobasic acids are univalent.

Bivalent elementary anions are those from sulphur, selenium, and tellurium in their metallic compounds, but the tendency to form ions is small. Many compound bivalent ions of dibasic acids are known.

No trivalent elementary anions are known. According to analogy, the nitrides of the metals are salts of trivalent nitrogen ion; solutions of them cannot be obtained, as they are decomposed by water into hydroxide and ammonia. Compound trivalent ions from the tribasic acids and their salts are numerous.

Elementary anions of higher valency are not known; compound anions, on the other hand, up to the sexavalent ion of mellitic acid. As a rule, it may be said that ions of high valency are formed with increasing difficulty.

Names and Symbols.—The names of the elementary ions are formed by the addition of the suffix -ion. The compound anions are named after their salts; thus the bivalent anion SO_4 is called sulphate ion. The suffix -ion denotes a substance, just as the ending acid or amine; just as one would say nitric acid is an oxidising agent, one would say nickel ion is green, and not nickel ions are green. The latter mode of expression is reminiscent of molecular hypotheses, which it is as well to avoid in an expression of actual behaviour, whether the hypothesis is considered probable or not.

The chemical signs of ions do not differ from ordinary chemical formulæ, so far as the elements and their coefficients are concerned. The ionic character, due to the electric charge, is indicated by adding a + or − sign. For typographical reasons, the common method of writing above the formula as many + or − as corresponds with the valency is to be avoided. The displacement of the line caused by the symbols $\overset{+++}{Fe}$, or $\overset{--}{SO_4}$, is not compensated for by any advantage. It is better to place the + or − to the right of the formula, as Fe^{+++}, or PO_4^{---}; the only disadvantage is that such typographical signs are not always available. The system generally adopted now is to replace the − by an acute accent ′, and the + by a dot ˙, ferric ion being written $Fe^{\cdot\cdot\cdot}$ and phosphate ion PO_4'''. This system will be made use of in this book.

The Ions of Water.—The hydrogen and hydroxyl ions play a special part. These univalent ions are the dissociation products of water, which, corresponding to its very small conductivity is dissociated to a very small extent (about 1 mol in 10^7 litres). Compounds which give hydrion (hydrogen ion) are acids; those which give hydroxidion (hydroxyl ion) are bases. While ordinary salts, or those which give neither hydrion nor hydroxidion, are dissociated in aqueous solution to about the same extent, there are very great differences among the acids and bases, the salts of hydrion and hydroxidion. There are all degrees from almost complete dissociation at moderate dilution to mere traces of it, *i.e.* up to the limits of experiment. Those which are dissociated to a large extent are the strong acids and bases—the others are weak. The characteristic properties of acids and bases depend upon their concentration of hydrion or hydroxidion, being directly proportional to the concentration.

The well-known action of acids and bases upon organic colouring matters, such as litmus, is due to these ions; the acid reaction signifies the presence of hydrion, the alkaline reaction that of hydroxidion.

Ionisation in Stages.—When a dibasic acid first undergoes dissociation the products are not the bivalent anion and hydrion, but the univalent anion RH' and hydrion according to the scheme $RH_2 = RH' + H^{\cdot}$, RH' further dissociating into R'' and $H^{\cdot}$. In a similar manner, a tribasic acid RH_3 gives the intermediate stages RH_2' and RH'' before the trivalent anion R''' makes its appearance. This is equally true of all compounds of multivalent ions; those ions are first formed which occasion the least separation into + and − electricity, or the least amount of dissociation; the further dissociation takes place in stages. Thus the number of different dissociation products of compounds of multivalent ions is great.

Formation of Ions.—The formation of ions from undissociated solid compounds occurs on liquefaction whether brought about by fusion or by solution. Very little is known regarding the first process, in spite of its theoretical simplicity; beyond the facts that the conductivity increases rapidly with rise of temperature, and that it is recognisable even in the solid state, there is nothing to be stated.

Our knowledge of the formation of conducting solutions rests mainly on aqueous solutions, which have been very thoroughly studied. The behaviour of other solutions has only recently been investigated to any extent.

Salts in the wider sense, which includes acids and bases, become electrolytic conductors when dissolved in water: they become dissociated into their ions. The dissociation is never complete, and always increases on dilution; as already stated it is considerable in the case of most neutral salts, generally exceeding 50 per cent, while in the case of acids and bases all possible degrees of dissociation occur. Temperature has not any great influence on the degree of dissociation. It acts in both directions, some substances being more dissociated, and others less dissociated, when the temperature is raised. These are questions of chemical equilibrium, and can only be fully discussed later.

In other solvents salts often possess conductivity, and are consequently dissociated, but usually to a much less extent than in water. Nearest to this solvent are the alcohols, especially those with few carbon atoms; also acetone, ammonia, and some other liquids. H C

The hydrocarbons, particularly the saturated hydrocarbons, and their halogen derivatives, and also the neutral ethers and esters all possess very slight dissociating power. The liquid organic acids, too, such as acetic acid (which in the pure state are practically non-conductors) have very little power of ionising dissolved substances.

Properties of Ions.—These are in the main those of their solutions, due allowance being made for the solvent. Thus, the ions of the light metals and of the halogens are colourless, since the solutions of all the salts formed by combination of these ions are colourless. Coloured ions occur among the heavy metals—that of nickel is green, of cobalt red, of copper greenish-blue, of manganese light pink, of bivalent iron pale green.

The properties of the individual ions can be determined only in a few cases, when the value for one ion is zero, as in the above example of coloured and colourless ions occurring together. When each ion contributes a definite amount to the property in question, there are, in general, no means of finding out what that amount is. For since the ions can only exist in equivalent amounts of opposite sign, any investigation of the property in a given solution gives the sum of the values which belong to the two ions. Attempts to obtain sufficient data for the calculation, by investigating solutions with one ion in common, are futile; there is always one variable too many, or one equation too few. Only in those cases in which one more datum can be ascertained by other means can the equations be solved, and the values estimated for each of the ions. A practical illustration is afforded by the question as to the contribution of each ion to the total conductivity of a solution in accordance with Kohlrausch's law; here the migration values supply the necessary datum.

The general relations between the velocities of migration of the different ions may be included here (*cf.* p. 390).

Of the univalent metallic ions, potassium, cæsium, and rubidium move most rapidly, and all three at about the same rate; sodium moves considerably more slowly, lithium still more so. Ammonium has the same velocity as potassium, and thallium is not far removed from these; silver comes very near sodium.

Amongst the bivalent kations, calcium, strontium, and barium move with nearly the same speed; magnesium is slower, and is followed closely by zinc, copper, and the other "vitriol" metals.

Very little is known regarding the migration velocities of trivalent and higher elementary kations.

Chloride, bromide, and iodide are among the fastest univalent anions and are almost equal in speed. Perchlorate ion, ClO_4, moves even more rapidly than these, and with decreasing velocity is followed by ClO_3, BrO_3, and IO_3. Nitrate ion resembles chlorate ion. Fluoride ion possesses a considerably smaller velocity, a property which seemingly belongs generally to the members of the natural families of the elements with low atomic weight.

The ions of the compound organic acids move more slowly the more atoms they contain. In comparatively simple radicals the nature of the elements is of decided influence; thus chlorine diminishes the velocity. But when the number of atoms in the radical exceeds twelve this influence disappears almost entirely. The velocity of migration then seems to depend only on the number of atoms, and decreases on the addition of new atoms more slowly, the more atoms there are already present.

It appears to tend to a limiting value, which for very complex anions and kations seems to be 10 to 12 units.

A constitutional influence is hardly recognisable in the organic isomeric anions, as they move with almost the same rapidity. But this influence is present in the isomeric kations of the substituted ammonium type (Bredig, 1892). The velocity of these isomeric ions is greater, the greater the number of hydrogen atoms which have been replaced; thus secondary amines are faster than primary, and quaternary ammonium bases have the greatest velocity of all. In general the velocity is greater, the more "symmetrical" the constitution of the ion.

The bivalent and multivalent radicals have been but little investigated. Selenate ion and sulphate ion have very nearly the same velocity, and so have phosphate ion and arsenate ion.

The influence of temperature does not vary much. It is mostly 2 per cent per degree; being somewhat larger with small velocities of migration, and conversely.

Isomeric Ions.—Isomerism, the difference of properties along with identical composition, is also found in ions. Here there are two essentially different kinds of isomerism. The one is the same isomerism which occurs in neutral compounds, since isomeric acids or bases form isomeric ions. In this sense, the ions of butyrates and of isobutyrates, and of trimethylammonium and propylammonium, are isomeric.

There is, in addition, a specific ionic isomerism, which has its origin in the different number of electric charges on the ion. In the first place, we have the elements and compounds which exist both in the neutral and in the ionic condition; and, further, there are the ions with the same composition and different amounts of electricity, and, therefore, with different properties. The latter case is considered first, as it is more in accord with older views.

Ionic isomerism due to differences of electric charge occurs more frequently with kations than with anions. Instances are those metals such as iron, chromium, tin, copper, thallium, and mercury, which form more than one series of salts. The mere fact that the analytical tests for the different series of salts are quite different shows that there are differences of ionic properties; indeed, the differences between ferrous and ferric salts, *i.e.* between $Fe^{\cdot\cdot}$ and $Fe^{\cdot\cdot\cdot}$, are greater than the differences between $Fe^{\cdot\cdot}$ and $Mn^{\cdot\cdot}$, or $Fe^{\cdot\cdot\cdot}$ and $Cr^{\cdot\cdot\cdot}$. The really close relation between them is that each of them can be converted into the other. To effect this, addition or subtraction of an electric charge is necessary; but since quantities of electricity can neither appear nor disappear without the simultaneous appearance or disappearance of an equal quantity of the opposite kind of electricity, this transition is necessarily accompanied by some other change. For instance, ferrous ion can be converted into ferric ion by leading chlorine into a solution of ferrous salt. $Fe^{\cdot\cdot}$ becomes $Fe^{\cdot\cdot\cdot}$, and at the same time Cl becomes Cl'; the neutral chlorine passes into the negative ion, if the positive bivalent ion is to become trivalent.

Accordingly, the process of oxidation in the wider sense (chemistry has long since extended the term oxidation beyond the taking up of oxygen) is, so far as ions and their derivatives are concerned, the gain of positive charges by the substance to be oxidised, or the equivalent loss of negative charges. Reduction means loss of positive charges or gain of negative charges. Those ideas will be applied later in the theory of the processes of the voltaic cell.

Elementary anions of different valency are not known. Among compound anions a particularly good example is that of manganate ion and permanganate ion. Both have the composition MnO_4, but the former is bivalent, the latter univalent. Along with this difference of charge there is the great difference in colour and other properties; the former is stable only in alkaline solution, the latter to a considerable extent in acid solution, the salts of the one are isomorphous with the sulphates, the salts of the latter are isomorphous with the perchlorates; permanganate ion is rightly considered an oxidation product of manganate ion, which has one negative charge more. A similar relation holds between the anions, $Fe(CN)_6$, of the ferrocyanides and ferricyanides; they have the same composition, but different properties, because the former is quadrivalent, the latter trivalent. Here, again, the trivalent ferricyanide ion is an oxidation product of the quadrivalent ferrocyanide ion, for it has one negative charge less.

If electrically isomeric ions differ so much because of the different number of charges, it is not surprising that still greater differences exist where the one form has electric charges, and the other has none. This is what holds with neutral substances and ions with the same composition. This isomerism or allotropism occurs both with elements and with compounds. The metals and halogens are examples of the one, hydrogen peroxide and cyanogen of the other. It is true that in the two last and the halogens there is also polymorphism, since the neutral substances have double the molar weight of the ions. But this is not so with the metals in which the molar weight is the same as the combining weight, and not a multiple of it.

The properties of the ions are widely different from those of the isomeric neutral substances. All one has to do is to bring to mind a solution of potassium iodide and the elements potassium and iodine, in order to realise how great the difference is. There is, however, a correspondingly great difference in the energy of the two states (p. 277). All the energy set free in the formation of a solution of potassium iodide in water from iodine, potassium, and water represents the loss of energy which the elements suffer on changing into the ionic state. For in a sufficiently dilute solution of potassium iodide there are present only iodine and potassium, both in the state of ions.

If this is kept in view, there should be no difficulty in realising that there is no equality between elements in the ordinary condition and as ions, and that none is to be expected. Neglect of this isomeric relationship has been the cause of most of the difficulty experienced by many people in dealing with these new views.

One important property of all ions remains to be mentioned. The existence of ions is bound up with the solutions, since they are first formed from the solid salt during the act of solution; if a substance leaves the solution, it loses at the same time the ionic condition. Thus, no ion can be volatile to a recognisable extent; this property belongs to neutral substances alone. Nor can an ion pass over to a solvent in which the formation of ions is zero. These properties, which are inherent in the ionic state, and are therefore common to all ions, condition many chemical peculiarities of ions. Occasion will be taken later to refer to some of them.

CHAPTER XVII

ELECTROLYTIC EQUILIBRIUM

Relation to the Phase Rule.—Electrolytic or ionic equilibrium differs from ordinary equilibria in the circumstance that in any phase the total equivalent concentrations of kations and anions must be the same. This is a necessary consequence of Faraday's law that equal quantities of electricity are united with chemical equivalents of different ions, in conjunction with the other laws that free electricity cannot exist in the interior of a conductor, and that the sum of all the positive and negative ionic charges must be zero.

In all cases of ionic equilibrium there is thus an additional equation, which reduces the degrees of freedom by one. In applying the phase rule, each kind of ion is to be treated as an independent component: notwithstanding this, the total number and also the degrees of freedom are diminished by one on account of the electrical condition. Complicated cases of ionic equilibrium can be conveniently treated, if due regard is paid to this rule.

If only one electrolyte is present, the phase rule is not altered. The two ions are to be counted as two components; but one is to be subtracted, so that the electrolyte may be treated as any other component. But it is different with two electrolytes. These may have one common ion, in which case three components are present, which are to be reduced to two. Or the four ions are all different, when the four components are to be treated as three. Other cases are treated in a similar manner.

An electrolyte which by itself dissociates into ions is an example of ionic equilibrium of the first order. This happens with fused salts: at ordinary temperature no moderately dissociated electrolyte is known. Denoting a kation by $K^{\cdot}$, an anion by A', the reaction equation for a simple binary electrolyte is $K^{\cdot} + A' = KA$, and the equilibrium equation $a_1 a_2 = kb$. Since the kations and anions must be of equal concentration, $a_1 = a_2$; if the concentration of the ions be denoted by a, then $a^2 = kb$, in which k is a function of the temperature and pressure, since one phase leaves two degrees of freedom.

In other words, every substance which dissociates into ions assumes, at any given temperature and pressure, an equilibrium state which depends only on the nature of the substance. The influence of pressure is small, since ionisation is accompanied by very small change of volume. The influence of temperature is defined by the rule that with rising temperature that reaction occurs which takes place with absorption of heat. Since, so far as is known, all substances which form ions in the absence of a solvent dissociate more at higher temperatures, the heat of formation of ions from them must be negative. Our knowledge in this matter is so limited that it is not possible to make any general statement.

Electrolytic Dissociation of Water.—Our most accurate knowledge in this respect relates to water. As the velocity of its ions are known from measurements on acids (hydrion) and bases (hydroxidion), its degree of dissociation can be obtained by dividing its conductivity by the sum of the two velocities.

In carrying this idea into effect, a difficulty is experienced in that the conductivity of even very carefully prepared water is due almost entirely to impurities, which have not been completely removed. With special precautions (vacuum distillation in a sealed-up glass vessel which had been used to contain pure water for over ten years) water was obtained, the conductivity of which to within 10 per cent was due to the water (Kohlrausch and Heydweiller, 1894). From this the conductivity of pure water could be calculated.

At 18° C. the specific conductivity of pure water is 385×10^{-10}, *i.e.* a 1 cm. cube has this conductivity in reciprocal ohms. The migration velocity of hydrion at this temperature is 313, that of hydroxidion 174, their sum, 487. Dividing the former number by this sum gives the concentration of the ions of water in mols per ccm.; this multiplied by 1000 gives the concentration in mols per litre. This comes to $\cdot 079 \times 10^{-6}$. Thus in 1 million litres of water at 18° there are ·079 g. of hydrion and 1·34 g. hydroxidion.

The concentration varies rapidly with temperature, since the heat of dissociation of water into its ions is very considerable, as calculated from the phenomena of neutralisation (p. 274). In the formula $d \lg k/dT = L/RT^2$, L is $= 57\cdot 5$ kj., $R = 8\cdot 31 \times 10^7$ and $T = 291$. This gives for $dT = 1$, $d \lg k = \cdot 082$, or since $d \lg k = dk/k$ the dissociation of water increases about 8 per cent for 1° C.

The following table gives the concentration of $H^{\cdot}$ or OH' in water in mols per million litres.

Temp.	0°	2°	10°	18°	26°	34°	42°	50°
Diss.	·034	·038	·055	·079	·106	·143	·188	·242

The dissociation of water has also been estimated in other different ways. These independent methods have led to concordant results, and constitute a remarkable confirmation of the theory of electrolytic dissociation.

Dissociation of Salts.—While our knowledge of ionic equilibrium of the first order does not go much further, the second order has been very fully investigated. The measurement of electric conductivity is so convenient and accurate a means of determining ionic concentrations, and, therefore, degrees of dissociation, that it has been applied to many substances, and a large number of results have been accumulated.

When an electrolyte is dissolved in water (aqueous solutions alone will be considered at present), it partially dissociates, and equilibrium is established, represented by the chemical equation $K^{\cdot} + A' = KA$, $K^{\cdot}$ being the kation, A' the anion, and KA the undissociated salt. If a_1, a_2 are the concentrations of the ions, and b that of the undecomposed part, $a_1 = a_2 = a$ as before. But while in the equilibrium of the first order these concentrations depend only on the temperature and the pressure, there is here one degree of freedom more, and one of the concentrations remains at disposal. For the experimental reason that the ions cannot be separately handled, the total concentration of the electrolyte, $a + b$, is the one which can be varied at will. The equation is $a^2/b = k$, and is in frequent use.

The concentration of the ions, a, is estimated in the same way as for water; the molar conductivity is compared with the limiting value for infinite dilution. If μ_v is the conductivity at the dilution v (1 mol in v litres), and μ_∞ the limit for infinite dilution, $\mu_v / \mu_\infty = a$ (p. 392) the ionised fraction, and a/v is the concentration of the ions, while $(1 - a)/v = b$, the concentration of the undissociated part. Putting these values in the equation we get

$$\frac{a^2}{(1-a)v} = k \text{ or } \frac{\mu_v{}^2}{\mu_\infty(\mu_\infty - \mu_v)v} = k$$

for the effect of dilution on the molar conductivity (Ostwald, 1888).

From this equation the following conclusions can be drawn. If a is very small, then $1 - a$ differs but little from unity, and the equation becomes $a^2 = vk$, the degree of dissociation and the molar conductivity are proportional to the square root of the dilution. This law was empirically deduced for weak electrolytes long before the theory of dissociation was established (Kohlrausch, 1878).

Then again, a increases with v, but not to an unlimited extent. The expression $a^2/(1 - a)$ becomes very great for very great values of v, since k is a constant. This is the case, for a approaches unity. The molar conductivity of all electrolytes increases with increasing dilution, approaching a maximum value which cannot be exceeded, as it is the value for the completely ionised electrolyte. This also was known before the theory was established (p. 388).

From the form of the equation the following conclusion can be drawn. The constant k is dependent on the nature of the substance, but we can always choose states of dilution v_1 and v_2 for two different substances so that the product v_1k_1 and v_2k_2 shall be equal. In that case $\frac{a^2}{1-a}$, and consequently a, must be the same for both, *i.e.* the conductivity with reference to the limiting value, or, what is the same thing, the proportion of dissociated molecules is the same for both substances. If we alter both dilutions in the same ratio, double them for example, the product v_1k_1 and v_2k_2 are still equal, and so also must be the values of a. From this it follows that the dilutions at which two substances are dissociated to the same extent are always proportional, independent of the absolute values of the dilution. This law was empirically discovered (Ostwald, 1885) before the theory of dissociation had been applied to electrolytes.

Finally the expression $\frac{\mu_v{}^2}{\mu_\infty(\mu_\infty - \mu_v)v}$ should be constant for any one electrolyte at all dilutions. This conclusion has been verified in the case of a very large number of electrolytes, both acids and bases. The following table for acetic acid at 25° will serve as an illustration.

v	μ	a	k
8	4·34	·01193	·0000180
16	6·10	·01673	179
32	8·65	·02380	182
64	12.09	·0333	179
128	16·99	·0468	179
256	23·82	·0656	180
512	32·20	·0914	180
1024	46·00	·1266	178
∞	364	...	...

The dissociation or equilibrium constant k has been determined for a large number of substances, and is closely related to their composition and constitution. These relationships will be reviewed further on.

Knowing the constant k, we can calculate the conductivity of an acid for any dilution. We have only for this purpose to solve the equation for a, when we obtain

$$\frac{\mu_v}{\mu_\infty} = a = \frac{-vk + \sqrt{v^2k^2 + 4vk}}{2}.$$

Temperature Effect.—The constant k varies with the temperature in accordance with the familiar formula $d \lg k/dT = L/RT^2$. Whether k increases or decreases with increase of temperature depends on the sign of the heat of dissociation L. If L is positive, *i.e.* heat is absorbed during dissociation, k increases with rise of temperature, if L is negative k will decrease. Now the sign and value of L can be determined for acids and bases; the method consists in measuring the heat of neutralisation of the substance with a strong base or acid. The difference between the observed value and the heat of formation of water from its ions, 57 kj., is L(1 – a), the product of the undissociated fraction of the substance and the heat of dissociation. If, then, the heat of neutralisation is less than 57 kj., the heat of ionisation is positive, and the dissociation increases with rise of temperature; if it is greater, the dissociation takes place with evolution of heat, and the dissociation decreases with rise of temperature.

When the heats of neutralisation of acids are looked at from this point of view, it is found that both cases exist; the heat of ionisation may be positive or negative. At first it seemed incredible that the decomposition of an acid into its ions should be accompanied by evolution of heat, for it was held impossible from a molecular standpoint that the separation of a molecule into its components should develop heat. But the decompositions of acetylene and of cyanogen into their components give out heat, and the apparent contradiction to the molecular hypothesis is a difficulty for that hypothesis, but not for the theory of ionisation.

These conclusions have been confirmed by measurement of the electric conductivity at various temperatures, from which a was directly calculated. It was shown that acids whose heats of neutralisation were too great were less dissociated at high temperatures. This effect is so great in the case of phosphoric acid and dichloracetic acid that, under certain circumstances, it exceeds the increase which the conductivity of all electrolytes experience owing to the greater velocity of migration of their ions at higher temperatures. These electrolytes show a temperature maximum of molar conductivity, *i.e.* with rise of temperature it first increases, as usual, and then decreases[1] (Arrhenius, 1888).

Abnormal Substances.—The equations and relations given above have been proved chiefly for monobasic organic acids, and have been fully established. Numerous bases, too, of the ammonia type afford complete agreement between theory and experiment. These electrolytes are as a rule not much dissociated, although agreement has been found in some cases in which the dissociation exceeded 70 per cent.

The behaviour of these electrolytes, all of which are characterised by moderate degree of dissociation, is governed by the law of mass-action, and forms a good illustration and confirmation of the law. But there is a large and important class of electrolytes which do not obey the law of mass-action. These are all largely dissociated in relatively concentrated solution, and on dilution their conductivity

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[1] It is often stated in text-books that electrolytes differ from conductors of the first class in this respect, that their conductivity increases with rise of temperature, whereas it decreases for the first class. From what is stated above, it is seen that no such rule is generally true for electrolytes. Nor does it hold for conductors of the first class.

increases more slowly than accords with the law of mass-action. If k is calculated in the usual manner it is not constant, but increases with increasing concentration. In this group we find almost all the neutral salts, the strongly ionised simple acids, such as the halogen acids, and also the strongly ionised bases, such as the hydroxides of the alkalies and alkaline earths.

The deviations in the conductivity of these substances from the dilution law are not large (several per cent if the observed and calculated values are compared), but they are too constant to be ascribed to accident. The cause has not been ascertained.

The deviations are so regular that several empirical formulæ have been proposed, which permit of the calculation of other values from any given conductivity at dilutions greater than 5 litres. In place of the theoretical formula $a^2/(1-a)v=k$, the formulæ $a^2/(1-a)\sqrt{v}=k$ (Rudolphi, 1895) or $a^3/(1-a)^2v=k$ (van't Hoff, 1895) express the behaviour of strong electrolytes with good approximation. A formal basis has been found for the second of these formulæ. The question whether the deviation is due to the conductivity not being a correct measure of the dissociation in this case must, it seems, be answered in the negative; the cause of the deviations may be found in some hitherto unnoticed energy participating in the equilibrium.

The Valency Rule.—On the other hand, certain empirical relations have been made out, which are of practical use in chemistry. Comparison of the effect of dilution on the equivalent (not molar) conductivity of salts, whose ions have different valency, shows that for the same dilution the change increases with the valency, and in normal cases proportionally to the product of the valencies of the two ions. As usually performed, the experiment consists in measuring the equivalent conductivity at 25° for the dilutions 32 and 1024 litres; the difference for a salt with two univalent ions is about 10 units, for a salt whose ions have the valency n_1 and n_2 the difference is $n_1n_2 \times 10$ units.

This rule is not general, for salts of polybasic acids with polyacid bases do not obey it, if these acids and bases are weak electrolytes. Salts of weak acids or weak bases do follow the rule if the other component is univalent and a strong electrolyte. The principal use made of this relation is to determine the basicity of an unknown acid or the "acidity" of an unknown base; it is easy in these cases to fulfil the necessary conditions.

In practice the pure acid is dissolved in 1/32 normal sodium hydroxide (or the base in 1/32 normal hydrochloric acid), and the conductivity measured of that solution, and of a solution thirty-two times more dilute. The difference of the two equivalent conductivities, divided by 10, gives the valency of the acid or base (Ostwald, 1887).

Analytical Application of Conductivity.—In conclusion, the measurement of electric conductivity is one of the most convenient and delicate aids to ascertaining the presence of a salt in solution, and determining the amount present if the nature of the salt is known. Since water can with care be prepared in the laboratory with a specific conductivity of 10^{-6}, solutions of about the same conductivity can be investigated with certainty. At such dilution the conductivities of neutral salts are additive;[1] the conductivity of the salt can therefore be ascertained by subtracting the conductivity of the water. The specific conductivity mentioned above corresponds to a neutral salt in 10^{-5} normal solution; concentrations down to this amount can be easily determined (Kohlrausch and Rose, 1893; W. Böttger, 1903; Kohlrausch, 1908).

In this manner the solubilities of the following "insoluble" salts have been determined; the numbers signify mols in one million litres. The figures given were found by W. Böttger for 20°; correction was made for the degree of dissociation.

	Silver.	Thallous.	Lead.
Chloride	10·6	13,600	34,600
Bromide	·45	1,640	22,700
Iodide	...	192	1,305
Thiocyanate	·83	12,000	13,900
Cyanide	1·50	...	...
Bromate	6700	9,950	28,900
Iodate	154	1,520	32·8
Oxide	180-216	...	58-92
Oxalate	120	31,800	6·1
Phosphate	15	...	·13
Sulphide	...	430	...
Carbonate	...	...	4·6-6·6
Sulphate	...	...	140
	Calcium Sulphate	15,000.	

The calculation depends on a knowledge of the migration velocities of the ions of these salts. The observed specific conductivity multiplied by 1000, and divided by the sum of the conductivities of the ions, gives the concentration in mols per litre.

Salts of Multivalent Ions.—The decomposition of a multivalent electrolyte into ions is more complicated than those already discussed. If, for example, a bivalent anion A'' is combined with two univalent kations $K^{\cdot}$, the process might be supposed to take place according to the equation $AK_2 = A'' + 2K^{\cdot}$. This is not the case; there are two processes, represented by the equations: $AK_2 = AK' + K^{\cdot}$ and

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[1] Acids and bases show great irregularities, which are due to neutralisation by the impurities; the $H^{\cdot}$ and OH', which are the most rapid, disappear, with a corresponding large decrease of conductivity. The true conductivity cannot be obtained by subtracting the conductivity of the water.

$AK' = A'' + K^{\cdot}$. The equilibrium equation is not $a^3/(1-a)v^2 = k$ as it would be on the first assumption; there are two equations. Denoting the ion $K^{\cdot}$ by a, AK′ by b, A″ by c, and the undissociated part by e, we have $a = b + 2c$, and $e = 1 - b - c$, from the reaction equations. The equilibrium equations are (1) $ab = k_1dv$ and (2) $ac = k_2bv$. Two of the values a, b, c, e can be eliminated, so that the final equilibrium equation contains two variables and the two constants k_1 and k_2. For a given value of one fraction, quite different values are obtained for the other fractions, according to the values for the two constants, which differ with the nature of the substance.

For the sake of clearness, let $K^{\cdot}$ be hydrion; the substance therefore is a dibasic acid. We will first consider the limiting case: k_2 very small compared with k_1. Then from equation (2) c is very small compared with b, and $a = b$, $e = 1 - a$. Introducing this in equation (1), we obtain

$$a^2/(1-a) = kv,$$

the usual dissociation equation for binary electrolytes. Dibasic acids of this type behave like monobasic acids. Only when v becomes very great does c in equation (2) attain to values which are too great to be neglected. This conclusion is in accord with experiment. The molar (two equivalents) conductivity of the weaker dibasic acids changes with dilution in precisely the same manner as monobasic acids do. We may take succinic acid as an example. The signification of the letters is as on p. 406. The value 356 has been taken

v	μ	a	k
16	11·40	·0320	·0000662
32	16·03	·0450	662
64	22·47	·0632	667
128	31·28	·0880	664
256	43·50	·1224	668
512	59·51	·1675	659
1024	81·64	·2295	668
2048	109·5	·3082	671

for μ_∞. The constant k proves to be the same for all the dilutions, although the final dilutions are very considerable.

With the stronger dibasic acids the dissociation of the univalent anion into hydrion and the bivalent anion begins much sooner. The value of k, calculated as usual, begins to increase when the second dissociation becomes noticeable. The following measurements on fumaric acid will make this clear:

v	μ	a	k
32	56·4	0·158	·00093
64	77·4	·217	94

v	μ	a	k
128	104·5	·293	·00095
256	139·0	·390	97
512	179·5	·503	99
1024	228·0	·639	·00110
2048	280·2	·785	140
∞	357·0	...	...

The values of k are accurate to about 2 per cent; the increase is recognisable at v = 256 litres, and is considerable at the remaining dilutions.

There is no necessary relation between k_1 and k_2, except that the latter must be the smaller. The values vary very much, depending upon constitutive properties of the acids which cannot be entered into here.

The same reasoning applies to the diacid bases, and has received experimental verification. Salts which give one bivalent and two univalent ions come into the same category, but as the simplest salts do not follow the law of mass-action, these can hardly be expected to do so; numerical adaptation of the formula is very complicated. The important point is that such salts undergo dissociation by stages, in consequence of which no direct conclusion can be drawn as to the degree of dissociation or the concentration of individual ions.

Still more complicated are the relations of salts both of whose ions are multivalent. It might be expected that if two ions of equal valency were present (as *e.g.* two bivalent ions in magnesium sulphate), the simple equation would be again applicable. There is the possibility to be considered of the occurrence of bivalent kations of the composition $AK_2^{\cdot\cdot}$, and anions of the type KA_2'' A_2''. For magnesium sulphate these ions would be $(SO_4)\ Mg_2^{\cdot\cdot}$ and $Mg\ (SO_4)_2''$. Observations on the connexion between conductivity and freezing-point depression indicate the existence of such ions in measurable quantity.

The weak tribasic and polybasic acids follow the simple law for binary electrolytes except that the irregularities begin to appear at smaller dilutions than is the case with dibasic acids.

Solid Phases.—We have now finished with the more important subject relating to a system of two ions. The answer to the question what effect the introduction of a solid phase has upon the equilibrium is that a solid substance, which in solution is ionised, goes into solution in precisely the same manner as unionised substances do. The solid is in equilibrium with the unionised part only, and this has the effect of making the apparent solubility of an electrolyte appear higher than the true solubility; by the latter is understood the concentration of the substance in solution which is in equilibrium with the solid phase. Any alteration in the equilibrium between the ions and the unionised part in the solution must find expression in a change of solubility.. This is the explanation of the remarkable fact that most sulphates of the magnesium sulphate type are almost quite insoluble in water at 200° to 300°, while, as a rule, solubility is greatly increased at such high temperatures. The heat of dissociation of these salts is positive; the degree of ionisation diminishes with rise of temperature, and the apparent solubility does the same.

Three Ions.—We must now take up solutions with three ions. Since the sum of kations and anions must be equal, this case arises when a solution contains two salts with one ion in common, *e.g.* two acids or two nitrates. The question becomes that of the mutual influence of each on the equilibrium between them. We can at once dispose of one case, that, namely, of all the electrolytes in the solution being fully dissociated or nearly so. They can then no longer influence each other, and the laws obtaining for the separate solutions may be applied to the mixture.

But if a highly dissociated and a weakly dissociated substance be simultaneously present in the solution, there will be mutual influence, if both contain one common ion. The formulæ of chemical equilibrium for quantities not equivalent then apply, and the state of equilibrium is different.

If we ask how two solutions must be constituted in order that the dissolved and partially dissociated substances may not influence each other, we must first of all demand that the active mass of the components shall not alter on mixing. Two solutions of the same substance will therefore not influence each other when their concentrations are equal, as indeed is *à priori* perfectly clear. The question is somewhat more complicated for two different substances containing a common ion, *e.g.* two acids. We shall consider for the sake of simplicity two monobasic acids HA_1 and HA_2. According to the general formulæ for chemical equilibrium these two equations will hold good—

$$K_1\frac{1-\alpha_1}{v_1}=\frac{\alpha_1}{v_1}\cdot\frac{\alpha_1}{v_1}$$

$$K_2\frac{1-\alpha_2}{v_2}=\frac{\alpha_2}{v_2}\cdot\frac{\alpha_2}{v_2},$$

where α is the dissociated portion and v the volume containing one mol.

If we mix the two solutions, the volume becomes v_1+v_2. The concentrations of the undecomposed portions fall to $\frac{1-\alpha_1}{v_1+v_2}$ and $\frac{1-\alpha_2}{v_1+v_2}$, while those of the acid ions fall to $\frac{\alpha_1}{v_1+v_2}$ and $\frac{\alpha_2}{v_1+v_2}$, and that of hydrion becomes $\frac{\alpha_1+\alpha_2}{v_1+v_2}$. The equilibrium equations for the two acids are thus

$$K_1\frac{1-\alpha_1}{v_1+v_2}=\frac{\alpha_1}{v_1+v_2}\cdot\frac{\alpha_1+\alpha_2}{v_1+v_2}$$

$$K_2\frac{1-\alpha_2}{v_1+v_2}=\frac{\alpha_2}{v_1+v_2}\cdot\frac{\alpha_1+\alpha_2}{v_1+v_2}.$$

If we divide each of these into the corresponding equation of the upper pair we obtain, after a little easy simplification,

$$\frac{\alpha_1}{\alpha_2}=\frac{v_1}{v_2}\text{ or }\frac{\alpha_1}{v_1}=\frac{\alpha_2}{v_2}.$$

Thus, in order that the states of dissociation of two acids be not altered on mixing, the concentration of hydrion must be the same in both solutions.

Thus, if we have acetic acid, for example, which is only slightly dissociated, and hydrochloric acid, which is highly dissociated, we must take very dilute solutions of the latter and moderately strong solutions of the former to get the same concentration of hydrion. From the table on p. 406 we see that acetic acid contains in round numbers ·012 mol of hydrion for a dilution of 8 l.; the concentration with respect to this ion is therefore $\frac{\cdot 012}{8}=\cdot 0015$ Hydrochloric acid will be without influence on this solution when the concentration of its hydrion corresponds to the equation $\frac{\alpha}{v}=\cdot 0015$. Since it may be considered completely dissociated at the requisite great dilutions, we have $\alpha=1$ and consequently $v=667$. The hydrochloric acid must therefore be of the concentration of one mol in 667 litres.

Isohydric Solutions.—Arrhenius, to whom the foregoing considerations are due (1888), terms such solutions as do not mutually alter their state of dissociation isohydric. Since, according to the formula just developed, it is only necessary for this that the concentrations of the same ion be equal, the absolute quantities of the solutions or their ratio playing no part, it follows that isohydric solutions leave each other undisturbed no matter in what proportions they may be.

Hence we conclude what will happen when two solutions not isohydric are mixed: they will so act on each other that they become isohydric. If we imagine the two solutions to be placed first in layers one above the other, we can remove water from the solution in which the concentration of the common ion is the smaller, and give it to the other solution, and go on doing so until the concentration in the two solutions has become the same. They are then isohydric, and can be mixed without any change in either taking place.

Two solutions isohydric with a third are isohydric with each other. For if two solutions are isohydric with a third, they each contain one ion at the same concentration as in the third, and thus have the same concentration themselves and are isohydric. This theorem was discovered experimentally before the theory showed it to be necessary.

Mutual Influence on the State of Equilibrium.—These relations afford an explanation of certain phenomena which have been made use of long before the reason had been ascertained. Thus the acid action of a weak acid is diminished to an extraordinary extent by the addition of its neutral salts. This could not be anticipated from the older theories, but is a necessary consequence from the ionisation point of view.

If a is the concentration of kation and anion in a solution of a weak acid, and c the unionised part, the equilibrium equation is $a^2 = kc$. If now a known quantity of a neutral salt of the same acid is added, the concentration of ion being b, the equilibrium is displaced, the concentration of the hydrion diminishing on account of the large increase in concentration of the anion. If a' be the concentration of hydrion in the new equilibrium, that of the anion $a' + b$, and the unionised part has increased to $c + a - a'$. The equation becomes $a'(a' + b) = k(c + a - a')$.

We have assumed that the acid is not largely dissociated; a and a' are therefore small compared with c, and unless the addition of neutral salt is very small, which is excluded, a' is also small in comparison with b. Neglecting the small quantities, we get

$$a'b = kc,$$

from which it follows that the concentration of hydrion is inversely proportional to the concentration of the added neutral salt. If we add an equivalent of sodium acetate (which we will assume to be completely ionised) to acetic acid of 8 litres dilution, where the degree of ionisation is ·012, with a concentration of hydrion ·0015, we have $b = 1/8$, $c = 1/8$; k is ·000018 (p. 406), from which $a' = kc/b =$ ·000018, which is about 1/83 of the concentration when no salt is added.[1]

On dilution of the solution, b the concentration of the salt, and c, the concentration of the unionised part of the acid, which is not very different from the total concentration of the acid, change in the same ratio, so that a', the concentration of hydrion, remains constant. While the concentration of hydrion in strong acids is inversely proportional to the volume, and in weak acids inversely proportional to the square root of the volume, we have here the limit, the concentration is practically independent of the

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[1] It is plain from the calculation that when an equivalent quantity of a neutral salt of the acid is added to a solution of a weak acid, the concentration of hydrion is equal to the dissociation constant, whatever the total concentration may be.

volume. This rule has a certain use, when it may be desirable to simplify the conditions in chemical reactions in which hydrion is concerned.

The use of sodium acetate in analytical work is based upon this equilibrium. This reagent is employed when it is desired to keep a liquid acid but at the same time to reduce the specific action of the acid. The precipitation of zinc sulphide, for example, is prevented by a very moderate concentration of hydrion; if sodium acetate is added, the concentration of hydrion is so strongly depressed that the precipitation is sufficiently complete to be used as a quantitative method. The precipitation of hot ferric solutions by addition of sodium acetate depends on the same principle. These phenomena cannot be taken up at present as they demand a knowledge of heterogeneous equilibrium.

This method is often employed in chemical kinetics, if it is desired to suspend the action of hydrion at a given moment, and yet not to make the liquid alkaline.

The same considerations apply to a weak, *i.e.* slightly ionised, base and its neutral salts. Further, a strong acid diminishes the ionisation of a weak acid, so that the anion of the latter almost disappears from the solution. The same holds for bases. This is occasionally made use of.

One Solid Phase.—If one solid phase makes its appearance in the equilibrium system comprising three ions, phenomena are observed which first received an explanation and numerical treatment after the establishment of the theory of ionisation (van't Hoff, Nernst). Consider the equation $ab = kc$ for the simplest case of binary dissociation, where a and b are the concentrations of the two ions, and c of the unionised part, there being, further, equilibrium between the latter and the solid phase. Thus c is a function of temperature only, and is constant for any given temperature. Accordingly ab is also constant, or a function of the temperature only.

In the solution of one electrolyte $a = b$. Addition of another electrolyte with a common ion increases a or b; the other must become smaller if equilibrium is to be retained. But this can happen only if some of the electrolyte separates as solid. The solution becomes supersaturated with respect to the solid.

This holds for either of the ions; the solubility of an electrolyte is greatest in pure water, and addition of another electrolyte with a common ion causes only a diminution of solubility.

This is well illustrated by the solubility of silver acetate. A saturated solution of this salt deposits crystals on addition of a concentrated solution of sodium acetate or of silver nitrate. No precipitation follows the addition of acetic acid, because it is only feebly ionised, and increases the concentration of acetate ion to a negligible extent.

This principle is of very great importance in analytical chemistry, for it provides a perfectly general method of diminishing the solubility of an "insoluble," *i.e.* sparingly soluble salt, to almost any extent, by keeping it in contact with a considerable concentration of one of its ions. The precipitating reagent of these sparingly soluble precipitated salts always contains one of the ions, hence the rule that more of the reagent is to be added than is necessary for the double decomposition. If barium sulphate has been precipitated from a sulphate solution by means of barium chloride, in order to estimate the amount of sulphate, an excess of barium chloride is added to ensure that barium ion is present in the solution, and that the sulphate ion has been brought to a minimum.

Washing the precipitate gradually replaces the solution with pure water, and the solubility of the precipitate increases. If it is small, the loss may be neglected; but if not, the washing must be continued with a solution containing the second ion. Obviously this must be a volatile substance, otherwise it cannot be removed from the precipitate by drying or heating. Ammonium magnesium phosphate, for instance, is washed with dilute ammonia, instead of with pure water. From the explanations made above, an easily volatile ammonium salt would be more efficient for this purpose, on account of its much greater degree of ionisation.[1]

In some instances there results an increase of solubility instead of the expected decrease, but in these cases it has been shown that other reactions have occurred between the ions, which have led to the formation of new substances (complex salts). Since each new substance is formed at the expense of those already present, the concentration of the latter must be diminished, and to restore the equilibrium more must dissolve to take its place.

Two Solid Phases.—The equilibrium of three ions in solution is absolutely fixed when two solid phases are present, *i.e.* two salts with one common ion (*e.g.* sodium chloride and ammonium chloride); such a system is in a definite state of saturation with respect to both solids. In other words, the same solution is obtained whatever the relative amounts of the two components provided they are both present as solid phases. The explanation is as follows. If both salts are in saturated solution, the equilibrium for the one is given by $ab = K$, where $K = kc$. For the second salt, with a common kation we will suppose, the equation is $ab' = K'$. Further, the sum of the concentrations of the two anions must be equal to that of the kation, or $a = b + b'$. There are thus three equations for three variables a, b and b′, and all three are absolutely defined.

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[1] More exact information on the applications of chemical equilibrium in analytical chemistry will be found in the author's *Wissenschaftlichen Grundlagen der analytischen Chemie*, 4. Aufl., Leipzig, 1904, or in the English translation, *Scientific Foundations of Analytical Chemistry*, translated by G. M'Gowan, London.

Since the constants K and K′ are functions of the temperature (and to a very small degree of pressure too) such a system has a solubility curve like that of a single substance, only here the composition of the solution is not known, unless two independent analytical data are known (any two of a, b, b′).

These results are amply verified by experiments, the results of which show that the total solubility of salts "which cannot interact," *i.e.* have a common ion, is independent of the relative amounts of the two salts in the solid state. In particular, there is no "displacement"; for instance, a large quantity of either of the salts may be dissolved in the common saturated solution by raising the temperature, but on cooling the solution to the original temperature, it all separates out again, and the composition of the solution is exactly the same as before.

Double Salts.—There are, however, certain pairs of salts in which "displacement" was formerly thought to occur. On more accurate investigation it was found that there are two different groups; in the one double salts are formed, in the other isomorphous solid solutions. In the latter we have a solid phase of varying composition; as this was expressly excluded in the present discussion, this group falls out of consideration.

The apparent "displacement" in the case of double salts was due to incomplete observation. If, for example, copper sulphate is added to a saturated solution of ammonium sulphate, and the solution allowed to crystallise, the composition of the solution will vary with the amount added. In this case, a double salt has been formed from the two components, and separates out as the only solid phase, unless so much copper sulphate has been added that it also appears as a solid phase. On the other hand, a saturated solution of copper sulphate will be changed in the same manner by addition of ammonium sulphate until solid ammonium sulphate appears along with the solid double salt. There are two saturated solutions; one in equilibrium with double salt and copper sulphate, the other with double salt and ammonium sulphate.

There is still a third saturated solution to be considered; that in which the double salt behaves as a single substance, where the composition of the substance in solution is the same as the double salt. Whether this solution is stable or not depends on the solubilities of the three solids; generally these are so changed by temperature that in certain regions (of temperature) the double salt exists in equilibrium with its saturated solution without decomposition into the single salts, while in the other regions the single salts are formed.

The following diagrams make this clear.[1] If for a given temperature the concentration of the one salt in the saturated solution is plotted on the abscissa, and the other on the ordinate (Fig. 60), A and B

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[1] Van't Hoff, *Bildung und Spaltung von Doppelsalzen*, Leipzig, 1897.

represent the saturated solutions of the single salts, and the two curves AF and BF the mixed solution in equilibrium with solid A and solid B respectively. At the intersection of the two curves, F, the solution is in equilibrium with both solid salts.

If there is a double salt, its solubility will be affected if one of the single salts is present in the solution, and to a greater extent, the more single salt there is in solution, since the concentration of the other salt must be correspondingly smaller. In the same diagram the solubility of the double salt in presence of excess of one component in the solution, is represented by the curve D. The point corresponding to saturation with respect to pure double salt is found by drawing through O a straight line at 45° to OB; at the point at which this line meets the curve D, the two co-ordinates representing the two components have the same value.[1]

If the curve D is quite outside AFB, as in Fig. 60, the solubility of the double salt is greater than that of either of the single salts, whether alone or in presence of the other salt in the solution, that is, the double salt solution is supersaturated with respect to the components. If nuclei are present, this solution will deposit one or other of the single salts, and will do so spontaneously when the metastable limit has been passed. At this temperature the double salt will decompose if brought into contact with water, the less soluble salt separating out.

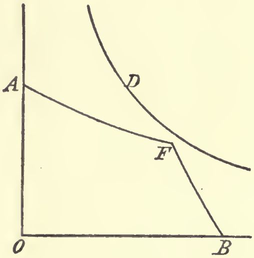

Fig. 60.

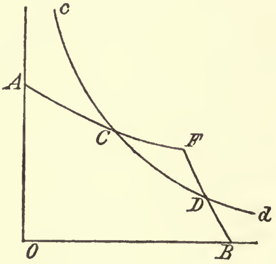

Fig. 61.

But if the curve D is situated as in Fig. 61, the solubility of the double salt between C and D is the smaller, and it is stable in contact with the solution.

Change of temperature will change the relative positions of the two curves, and at some temperature the point F will be common to them both. Then at F the double salt is in equilibrium with the solution and the two solid single salts, and we have a "condensed equilibrium," as regards the solids or a transition point.

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[1] It is assumed that the double salt contains an equal number of mols of the two components.

If the double salt is brought into contact with water at this temperature, what is formed is not a simple saturated solution of the double salt. The composition of this would be given by p_1 (Fig. 62), since the composition of the solution is the same as the double salt only on the line OP. What does happen is that the double salt undergoes partial decomposition, that component separating out which is present in least quantity in the solution. Not until the solution has in this way attained the composition represented by F, can the double salt remain unchanged in contact with the solution.

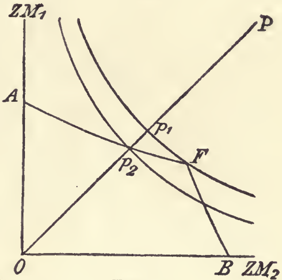

FIG. 62.

At the temperature at which the solubility curve of the double salt passes through p_2, the double salts can dissolve in water without one of the components separating out in the solid state. Between p_2 and the intersection of the double salt curve and BF there is a region of double salt equilibrium. The two intersections represent two equilibria with two solid phases; double salt along with each of the single salts. Beyond them are solutions containing an excess of a single salt, which separates in the solid state, the double salt being decomposed.

These considerations might be extended in various directions; as to these van't Hoff's book should be consulted.

Four Ions.—We will now proceed to the case of four different ions together in solution; and may state at once that all possible combinations of them will form undissociated salts. All the possible salts will be formed, but only to a small extent, the greater part of the ions remaining as independent ions. Certainly there is no question of the strong acids uniting with the strong bases to any considerable extent, as, without any experimental proof, used to be assumed.

We have here two groups; in the one, three ions of one kind and one ion of the other (as, for example, three different kations and one anion), or two kations and two anions. The first group can be treated in a way analogous to that of p. 414 *seq.*; no special interest attaches to it. The second group represents an old problem which has occupied general chemistry for hundreds of years; the decomposition of a salt by an acid, and the double decomposition between two salts.

Before proceeding to quantitative treatment, we shall endeavour to give a general idea of the essentials of these phenomena, more especially as the point of view afforded by the theory of ionisation differs in many respects from that of the earlier theories.

As was formerly remarked, solutions of almost all salts are highly dissociated, as are also those of the strong mineral acids. If we mix a dilute solution of hydrochloric acid, which contains the free ions $H^{\cdot}$ and Cl' almost exclusively, with a dilute solution of a salt, which we may denote generally by MA, M being the kation and A the anion, then for equilibrium it is necessary that all positive and negative ions should be in dissociation-equilibrium with respect to the possible compounds. Should the acid of the salt in the free state be likewise highly dissociated, equilibrium between the hydrion of the hydrochloric acid and the anion A will be already approximately existent. If, however, the acid HA is only dissociated to a very slight extent, like acetic acid, the hydrion of the hydrochloric acid and the acid radical will act on each other so as to form undissociated molecules HA, until the remaining hydrochloric acid becomes isohydric with the acid HA formed. The result is thus that a certain quantity of the acid HA is formed at the expense of the salt MA and the hydrochloric acid, the amount being greater the less the acid is dissociated, *i.e.* the weaker it is.

This in the light of the theory of dissociation is the process hitherto known as the displacement of a weak acid from its salt by a stronger acid, and ascribed to a special chemical force of affinity between the metal and the various acid radicals. We see that the cause lies in the nature of the acid; the metal of the salt plays but a small part, for it only serves by its presence to keep the ion of the acid in the dissociated state. Thus is explained the empirical law (Ostwald, 1878) that the ratio in which one acid is "displaced" from a salt by another does not depend on the nature of the basic component. The active component, *i.e.* the one which undergoes change during the reaction, is not the strong acid but the weak one. Its tendency to go into the undissociated state is the only cause of any reaction taking place.

We may now represent another process in the same way—namely, the neutralisation of an acid by a base. If a salt is dissociated into its two ions, it appears at first sight incomprehensible why an acid and a base should act on each other in any way, since their two active components, the metal and the acid ion, do not enter into combination with each other at all.

This is perfectly correct, however; salt-formation in aqueous solution is in reality not a combination of these components of acid and base, but consists in the combination of the two other components, the hydrion of the acid with the hydroxidion of the base. Water is an electrolyte of extraordinarily small dissociation. Consequently it is impossible for the ions of water to exist uncombined in the same liquid, and so, when they meet, they immediately unite to form water. The process of neutralisation in aqueous solution is thus nothing but a formation of water (p. 274).

The General Equilibrium Equation.—We must now fix quite generally the conditions for the establishment of chemical equilibrium between four ions, two anions A_1, A_2, and two kations B_1, B_2. These conditions may be expressed in the following theorem: If isohydric solutions of A_1B_1, A_1B_2, A_2B_1, A_2B_2 be prepared (A_1B_1 being made isohydric with A_1B_2, this with A_2B_2, and this again with A_2B_1), then when these are mixed in such volumes a, b, c, d that the equation

$$ad = bc$$

holds good, the substances are and will remain in equilibrium (Arrhenius, 1890).

If we denote the undissociated quantities of the four substances by α, β, γ, δ, and remember that the dissociated portions are proportional to the volumes (for according to hypothesis the solutions are isohydric), and can thus be denoted by ha, hb, hc, hd, where h is a constant, then the equations for equilibrium will be as follows:

$$k_1\frac{\alpha}{a} = \left(\frac{ha}{a}\right)^2, \quad k_2\frac{\beta}{b} = \left(\frac{hb}{b}\right)^2, \text{ etc.}$$

or

$$k_1\alpha = h^2a, \qquad k_2\beta = h^2b, \text{ etc.}$$

If we now imagine the four volumes a, b, c, d to be mixed, new conditions of equilibrium will appear, the equations assuming the following form:

$$k_1\frac{\alpha}{a+b+c+d} = \frac{h^2(a+b)(a+c)}{(a+b+c+d)^2},$$

$$k_2\frac{\beta}{a+b+c+d} = \frac{h^2(b+a)(b+d)}{(a+b+c+d)^2}, \text{ etc.}$$

For in the mixture the undissociated quantity of A_1B_1 is as before α, but it is now contained in the volume $a + b + c + d$. Of the dissociated portions A_1 and B_1 the quantity a of A_1 comes from the solution A_1B_1 and the quantity b from the solution A_1B_2; of B_1 we have a from A_1B_1 and c from the third solution A_2B_1; each quantity must again be divided by the total volume in order that the concentration may be obtained. The other equations follow in a similar manner.

On reduction they give

$$k_1\alpha = \frac{h^2(a^2+ab+ac+bc)}{a+b+c+d}; \quad k_2\beta = \frac{h^2(b^2+ab+bd+ad)}{a+b+c+d}, \text{ etc.}$$

Now, in order that the state of dissociation of the four substances shall be unchanged it is necessary that the relations between a and α, b and β, etc., remain as in the original solutions. From these and the above equations we obtain by division:

$$a = \frac{a^2 + ab + ac + bc}{a + b + c + d}; \ b = \frac{b^2 + ab + bd + ad}{a + b + c + d}, \text{ etc.}$$

whence $$ad = bc; \ ad = bc, \text{ etc.},$$

i.e. in order that the state of dissociation may remain unaltered the condition

$$ad = bc$$

must be fulfilled.

But the volumes a, b, c, d, are proportional to the active or dissociated portions of the various electrolytes, a and d belonging to the substances A_1B_1 and A_2B_2, which by their mutual action give A_1B_2 and A_2B_1. The dissociated quantities are again proportional to the total quantities, p_1, p_2, q_1, q_2, each multiplied by the respective factor of dissociation, m_1, m_2, m_3, m_4. Consequently we get the following formula for equilibrium:

$$m_1p_1 \cdot m_2p_2 = m_3q_1 \cdot m_4q_2.$$

This is not only a representation of Guldberg and Waage's law of mass-action (pp. 307 and 337), for which we put $m_3m_4/m_1m_2 = K$, but it also contains the extension discovered by Ostwald (1875) that each of the coefficients falls into two factors, one of which depends only on the acid, and the other only on the base, or, more accurately, one only on the positive ion and the other only on the negative ion.

The equation, however, goes beyond this empirical relation. It show that the coefficients m_1, m_2, . . . which in the former equations were, as a first approximation, looked upon as constant, are in fact not so. The coefficients of dissociation depend not only on the nature of the substances themselves, but also on the presence of other substances containing the same ion, and from this last circumstance are subject to considerable variation. In this we find the explanation of the various exceptions from the law of mass-action in the form containing the two coefficients as constants.

The application of this formula to calculate the different equilibria between four conjugate electrolytes cannot be detailed here. It can be immediately shown that the dissociation of a weak acid in presence of a strongly dissociated electrolyte takes place as if the latter were the neutral salt of this acid; its dissociation is thus inversely proportional to the concentration of this foreign substance (p. 414). It can further be shown that in the "competition of two acids for a base," *i.e.* the equilibrium between two anions, hydrion and one other kation, all in equivalent proportions, the base is divided between the acids in the ratio of their degree of ionisation at the given dilution. Or, if solutions are prepared, each of which contain one of the acids and its neutral salt in the given proportion, no reaction takes place on mixing them.

These relations are interesting from the point of view of the older attempts to determine the relative "strength" of acids, and have been mentioned on that account; they cannot be more fully discussed here.

Hydrolysis.—A very important case of equilibrium between four ions arises in solutions of simple salts if the ions of water participate to a measurable extent in the equilibrium. This can only happen if one at least of the ions of the salt forms with the hydrion or hydroxidion of the water a compound whose degree of dissociation is comparable with that of water (p. 404), *i.e.* when the salt is derived from a very weak acid or base.

To gain an insight into the phenomena in question, we will consider the sodium salt of a very weak acid, say, phenol. Phenol ion forms with hydrion the very feebly ionised compound phenol; an appreciable quantity of this compound will be formed when, in the form of a salt, a large number of these ions are brought into solution. This can only take place if an equivalent amount of hydroxidion is set free from the water, and, in consequence, the solution will contain a measurable amount of hydroxidion as well as of phenol. On account of the latter the solution smells of phenol (ions are not volatile, therefore have no odour, and the odour must come from free phenol), and owing to the hydroxidion it has an alkaline reaction. For the alkaline reaction, peculiar to solutions of bases, is due to their common component, hydroxidion.[1]

It is thus seen that in the solution part of the phenol and the sodium hydroxide, from which sodium phenolate is formed, are not united but remain free. As they were in combination in the solid, they have been dissociated by the water into acid and base. This process is hydrolysis.

The same process occurs with the compounds of strong acids and weak bases; the solution has an acid reaction, because a certain amount of hydroxidion has been used in forming undissociated base from the salt, and the equivalent amount of hydrion has been formed. Properties of the uncombined base will also be found in the solution, as is the case with aniline hydrochloride.

If both components of the salt are weak electrolytes, the above considerations only apply in part, viz. that relating to the formation of the unionised compound from the ions of the salt and of water. Both ions are used up in this case, so that the liquid is neither acid nor alkaline in reaction. This, of course, is only strictly accurate if

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[1] The theory of indicators is dealt with below.

the two substances have the same dissociation constant; if they have not, the one with the larger constant determines the reaction of the solution towards indicators.

The calculations are as follows:—Let the concentrations be: anion = a, hydrion = h, kation = b, hydroxidion = y, unionised acid = S, unionised base = B; the equations are: $ah = k_1S$, $by = k_2B$, $hy = K$. The first equation gives the relation between the anion and hydrion of the acid, k_1 being the dissociation constant of the acid. The second is the corresponding equation for the base. The third represents the equilibrium between hydrion and hydroxidion and water; K is the dissociation constant of water, the value of which, calculated from the concentrations of the two ions given on p. 404 ($\cdot 079 \times 10^{-6}$ at 18° C.), is $K = 0\cdot 61 \times 10^{-14}$.

For a salt of a weak acid and a strong base (*e.g.* sodium phenolate), combination of the first and third equation gives $yS/a = K/k_1$. Now y is the concentration of hydroxidion; if neutral salt has been dissolved, S, the concentration of liberated acid (which is practically undissociated) is also equal to y; a, the concentration of anion, is the same as that of the salt, as it is completely ionised. K and k_1 are constants. The hydrolysis is measured by the value of y; the equation is of the form $y^2/a = k$ (where $k = K/k_1$), which is the same as for the dissociation of a weak acid or base; for slight hydrolysis, the extent is inversely proportional to the square root of the concentration, with greater hydrolysis more slowly than this and the ratio of the square of the hydrolysed part to the non-hydrolysed part is constant.

It is apparent from the original equation,

$$yS/a = K/k_1,$$

that y can be diminished to any extent by increasing S, and a moderate increase of S, *i.e.* a small excess of undissociated acid, is sufficient to correspondingly diminish y. A solution of sodium phenolate at a dilution of 10 l. is hydrolysed to ·08; addition of an excess of ·08 phenol reduces the hydrolysis to ·05. Since this excess is practically unionised, it has no effect on the conductivity, and in this way the true value of the migration velocity can be determined for ions whose salts are hydrolysed (Bredig, 1894).

The same considerations and formulæ hold for salts of strong acids and weak bases.

It is quite different if both acid and base are weak. In $yS/a = K/k_1$, the concentration of hydroxidion is no longer equal to the amount of hydrolysis, but the liberated base is only slightly ionised, as it is in the presence of its neutral salt. But the relation holds here (p. 415) that the concentration of hydroxidion is independent of the dilution: y is therefore a constant, and S/a becomes a constant. Consider a solution containing equivalent quantities of acid and base, S is the concentration of the unionised free acid, and gives therefore the amount of hydrolysis, while a, the concentration of the anion, gives the amount of salt which is not hydrolysed, since the salt was supposed to be completely ionised. The equation $S/a = \text{constant}$ states that the ratio of the hydrolysed fraction of the salt to the undecomposed part is independent of the concentration.

These results for two weak electrolytes stand in the same relation to the previous case of one weak electrolyte, as that existing between the dissociation of a weak acid with or without the presence of its neutral salt; the hydrolytic or electrolytic dissociation is in the one case independent of the dilution, in the other it is proportional to the square root of the dilution.

It must be noted that these statements, like the formulæ, only apply to compounds of univalent ions. They have been worked out in many cases for multivalent ions; the more complicated relations need not be given here. Further, the rules given above are only approximations obtained by making certain simplifying assumptions which have been stated in each case. The real behaviour shows more or less divergence from them; still most of these theoretical results have been compared with experimental results, and found to be so far in agreement with them, that they may safely be considered as experimentally confirmed.

Theory of Indicators.—A theory of acidimetric and alkalimetric indicators can be based on the foregoing principles (Ostwald, 1894). These are colouring matters, which change colour when the solution changes from acid to alkaline; it is well known that they behave differently, certain of them being suitable for some acids or bases, and others not.

An alkalimetric indicator is always an acid or a base, whose ion has a different colour from that of the undissociated substance. There are thus two classes of indicators. We will consider the acid ones first.

A coloured acid cannot be used as an indicator if it is quite a strong acid. If it were, it would be already ionised at the dilution at which an indicator is employed, and could show no change of colour since the ions would remain unchanged on neutralisation, *i.e.* formation of the salt; the ion MnO_4' of the permanganates is an example. But if the acid is weak, it will be in the ionic state in the solution if there is excess of base, *i.e.* in presence of much hydroxidion and vanishingly little hydrion. When more and more acid is added, a point is reached at which the hydroxidion is almost used up by the added hydrion, and a slight excess of hydrion is present. This will unite at once with the anion of the indicator, which then changes into the colour of the undissociated compound.

Thus the anion of phenolphthalein is red, the undissociated compound is colourless.[1] The anion of litmus is blue. The undissociated substance red, etc.

Now phenolphthalein can be used to titrate weak acids, but only with a strong base, as *e.g.* barium hydroxide. It is useless in presence of a weak base, such as ammonia, for there is no sharp colour change, only a gradual transition.

The reason is that it is a very weak acid; its salts with weak bases are therefore hydrolysed, and before hydrion is present in any excess an increasingly greater proportion of the ions have been converted into the colourless undissociated compound. If the base is strong, the hydrolysis is very slight, and the colour change is sharp.

To titrate a weak base with an acid indicator, recourse must be had to a stronger acid, which will not be so much hydrolysed. Methyl orange, the sulphonic acid of dimethylamidoazobenzene, is such an indicator. The ion is yellow, the compound is red; these are the colours in alkaline and acid solutions.

Weak bases may be titrated with methyl orange, but only with strong acids, such as hydrochloric acid or sulphuric acid. With weak acids, like acetic acid, the colour change is indefinite. The explanation is that the first slight excess of acetic acid, being in presence of its neutral salt, gives very little hydrion, so little in fact that it is not sufficient to unite with the ion of the indicator. There results a chemical equilibrium, which is gradually displaced on increasing addition of acetic acid with production of an undissociated indicator, but this is spread over so wide a region of concentration that exact measurement is impossible.

Hence the following rules: weak acids must be titrated with a strong base and a weak acid indicator; weak bases with a strong acid and a moderately strong acid indicator.

Similar considerations hold for basic dye-stuffs, which can be used as indicators when the ion and the substance have different colours. But the rules are to be inverted: weak acids require a strong basic indicator, weak bases as weak a basic indicator as possible.

Phenolphthalein is one of the weakest acid indicators. It is followed by litmus, cochineal, rosolic acid, nitrophenol, and finally methyl orange as the strongest acid employed as an indicator. Basic indicators are not much in use.

The Solubility Product.—To the electrolytic equilibria in a liquid already dealt with are to be added those in which several phases appear. Those with solid phases are the most important; the

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[1] The question has often been raised recently, whether the neutral indicator does not undergo an isomeric rearrangement, as seems probable from certain theories as to the constitutive nature of light-absorption and colour. It may be left to the future to settle this question, which is as yet doubtful; in any case the foundation of the theory outlined above is not affected by it.

question under what circumstances a precipitate occurs in the double decomposition of two salts, has occupied the attention of chemists since the times of Stahl and Bergmann.

In conjunction with the statements on p. 326, it may be said generally that every solid salt has a definite solubility at any given temperature, which is defined by the concentration C of the unionised part in the solution. This quantity, again, is fixed by a and b, the concentration of the ions in the solution. The relation between the three is given by the equation $a^m b^n = kc$, where m and n are the number of ions in the salt. If the magnitude $a^m b^n$ is called the solubility product, precipitation becomes possible in a solution, so soon as the solubility product is exceeded.[1]

If, therefore, two ions which can form a salt with a small solubility product, are brought together in solution, supersaturation will exist, and precipitation will set in if the metastable region is exceeded or nuclei are present. This simple rule embraces the whole theory of precipitation in the reactions between electrolytes.

Simple cases such as arise in the reaction between the ions of neutral salts, require no elucidation; *e.g.* the precipitation of calcium salts by ammonium oxalate, of sulphates by barium or lead salts.

It is more difficult when one or other of the electrolytes is not completely ionised, as most neutral salts practically are. Among these are the precipitations by acids, which formerly caused some difficulty. While all calcium salts are precipitated by sulphuric acid, the precipitation of calcium acetate by oxalic acid is practically complete, but not of calcium nitrate, and the presence of free nitric acid can prevent the precipitation altogether.

The reason is as follows: sulphuric acid is a strong acid, while oxalic acid belongs to the weaker acids. If hydrion is present in solution along with sulphate ion, they unite only to a very slight extent to form sulphuric acid. But with oxalate ion combination is extensive when excess of hydrion is present. Oxalate ion disappears from the solution, and a point is soon reached where the solubility product is not reached.

Hence the rule that acids can hinder the precipitation of sparingly soluble salts of weak acids, but not of salts of strong acids.

This conclusion is generally borne out by experience; the silver halides are practically insoluble in other acids, because the halogen acids are among the strongest acids. On the other hand, the salts of the weak phosphoric acid and of the still weaker carbonic acid are soluble not only in the strong mineral acids, but most of the salts of the former and all the salts of the latter dissolve in acetic acid.

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[1] If the excess is not great, precipitation does not necessarily occur, if the supersaturation is still in the metastable region. But if precipitation has commenced, it proceeds to the equilibrium point.

The same considerations govern the question, which precipitates are soluble in acids, and which are not.

The precipitation of sparingly soluble acid or basic substances follows the same rules. The former is not a common occurrence, but the latter is very frequent and may be further considered.

When potassium hydroxide is added to a solution of a copper salt, the concentration of hydroxidion is increased, and soon the solubility product cupric ion × hydroxidion is exceeded, and cupric hydroxide is precipitated. This is the typical reaction. Irregularities occur, for instance, in the precipitation of magnesium salts with ammonia. Precipitation is incomplete, and if ammonium salt has been previously added, does not take place at all.

The solubility product of magnesium hydroxide is moderately large, as may be known by its slight alkaline reaction. Ammonia is a weak base, and the concentration of hydroxidion in solution is not large. Still it is enough to exceed the solubility product of magnesium hydroxide when the two solutions are mixed. During the reaction ammonium ion increases in the solution, for a strongly ionised salt is formed with the anion of the magnesium salt; this depresses the ionisation of the ammonia (p. 414) with corresponding diminution of hydroxidion. At the same time, the concentration of magnesium ion has diminished owing to the separation of the hydroxide; and, in consequence, the solubility product is not reached even on further addition of ammonia, *i.e.* no further precipitation takes place. Previous addition of ammonium salt will reduce the concentration of hydroxidion in the ammonia to such an extent that the solubility product of magnesium hydroxide is never reached.

In general, any process which removes one of the ions of a precipitate from the solution, will favour its solubility. It is known that silver chloride is markedly soluble in mercuric nitrate. This is because mercuric chloride is a feebly ionised salt; the chloride ion unites with mercuric ion from the nitrate to form unionised mercuric chloride, and more silver chloride goes into solution until the increased concentration of silver ion has made good the loss of chloride ion, and the solubility product is again reached.

Complex Compounds.—One of the commonest ways in which ions are removed from solution is by the formation of "complexes." This name is given to ions in which components occur which are not there as ions, although they can exist as ions. Theoretically these compounds are always split up to some extent into the simple ions, although the greater part is present as complex; frequently this decomposition is experimentally recognisable.

Almost all silver salts are soluble in potassium cyanide, because silver ion unites with cyanide ion to form the complex anion $Ag(CN)_2'$. The concentration of silver ion in the solution becomes very small, and large amounts of the solid salt must go into solution to increase the concentration of the anion if the solubility product is to be reached.

Similar instances are very frequent.[1] They are known in analytical chemistry as anomalous reactions; this term may almost be considered synonymous with formation of complexes. At any rate, the increased solubility of a sparingly soluble salt (in its widest sense) is almost always to be referred to the entrance of one of its ions into a compound in which it is not an ion.

Order of Separation of Salts.—These considerations throw light on the question, which of the four possible salts will separate out from a solution containing two kations and two anions. It is that one whose solubility product is first reached as the solution is concentrated. The same holds for the other salts, only the matter is more complicated because the separation of the first salt has diminished the concentration of these ions, so that, owing to the accumulation of the other two ions, it is generally the salt of these ions whose solubility product is next exceeded.

Complete equilibrium is not established by the separation of two salts, for a system of four ions requires three solid phases, along with liquid and vapour, for an absolutely defined relation between temperature and composition of the solution.[2] The solution will have the character of a saturated solution only when three of the four possible salts are present as solids; *i.e.* will undergo no change when the quantities of the solid phases are altered. If two salts, all of whose ions are different, are brought into excess of water, equilibrium is not established by the mere process of solution. For this, one of the two salts produced by double decomposition from the first two must separate out as a solid.

Which of these salts will be formed, depends on the solubility products of the two. These may change place with change of temperature, so that in general there is one definite temperature at which all four salts can coexist. Below this transition temperature, the one triad is stable, above it the other.

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[1] Details will be found in the author's *Wissenchaftlichen Grundlagen der analytischen Chemie*, 4. Aufl., Leipzig, 1904 (or the English translation, *The Scientific Foundations of Analytical Chemistry*, London).

[2] Four ions and water give 5 components, therefore 7 degrees of freedom, according to the phase rule. These are reduced by the ionic equation (p. 403) to six; for one degree of freedom to remain, five phases (three solid, liquid, and vapour), must be present.

CHAPTER XVIII

VOLTAIC CELLS

General.—After Galvani had discovered the jerking of prepared frog limbs which occurs when muscle and nerve come in contact with metals, and Volta had shown the necessity for two metals and had demonstrated the purely electrical nature of the phenomena, the question as to the source of this electricity immediately arose. Galvani sought it in living cells, Volta in the contact of two different metals. Volta in a series of brilliant researches succeeded in proving that Galvani's views were wrong; there then arose a dispute as to his own theory which lasted over half a century, echoes of which may still be heard. The law of energy settled this question, as it has so many others: it immediately showed what the question was. By the construction of his "pile" Volta showed that an apparatus could be made by alternating discs of two different metals with a moist conductor, which would perform all kinds of thermal, chemical and mechanical work. The first question with regard to it ought to have been, "Whence comes the electric energy?" not, "Whence comes the electricity?" The work which the pile could perform must arise from some ulterior source of energy, and the only available source was the chemical processes in the pile.

The settling of the question was rendered more difficult by the great disproportion between the quantity of electricity and of matter which move together in accordance with Faraday's law. Quantities of electricity which can charge large condensers so as to give long sparks, are combined with scarcely weighable amounts of their carriers, the ions: thus it is possible to have important electrical effects, and no possibility of evidence of the corresponding chemical processes. But since Faraday's law has been shown to be so exact a law of nature that up to now no deviations from it have been discovered, it can be said with certainty that in systems containing electrolytes, no electrical process can occur without a corresponding chemical process.

A Voltaic element is a machine which converts chemical energy into electrical energy. In a theoretically perfect machine of this kind, the chemical and electrical processes will be so bound together that neither of them can proceed without the other. Such a machine fulfils the conditions for reversibility, and allows the corresponding laws to be applied.

One cause of the very slow development of a rational theory of Voltaic elements was that the cells at first in use were far removed from this ideal; and indeed were not connected with any sharply defined chemical process. In the original cell of Volta, zinc, silver and salt water were employed. Ritter substituted copper for silver, and Fechner noticed that the copper worked best if its surface was oxidised. All these cells had a variable electromotive force; they become "polarised" in use. This was because the chemical process at first consisted in reduction of the cupric oxide; when this was used up hydrogen was liberated, and this diminished the electromotive force.

Measurements.—Electrical energy (p. 379) is measured by the product of quantity of electricity and electromotive force. Faraday's law accounts for the former: 96540 coul. go through the cell for every equivalent (*i.e.* to 1 g. hydrogen) of reacting substance, independent of the nature of the cell. The difference of energy of various cells must therefore be expressed exclusively by the electromotive force, the measurement of which is the foundation of its estimation. The best method of measuring electromotive force is to prepare a known series of electromotive forces, and oppose them to the unknown one. When two exactly balance each other, the unknown electromotive force is the same as the one which compensates it (Poggendorf, 1842).

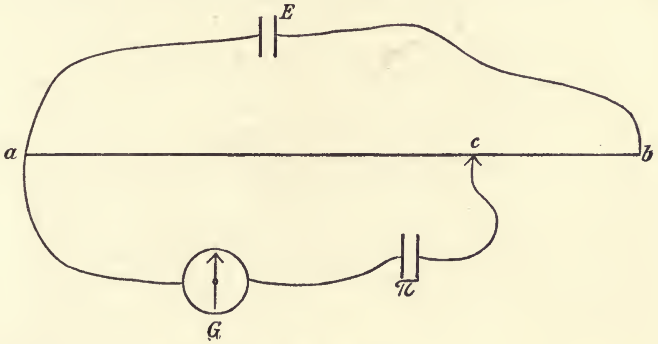

FIG. 63.

Now that accumulators give a very steady current, it is easy to set up a suitable apparatus. An accumulator E, Fig. 63, is connected to a wire stretched over a metre scale (the measuring bridge for conductivity determinations, p. 386, is suitable), and the cell to be measured is connected with a current or potential indicator G, in a circuit which ends in the sliding contact C. The latter is moved until G gives no movement; the reading of c in millimetres gives the electromotive force π in thousandths of that between a and b.

G may be either a sensitive galvanometer or an electrometer: the latter has the advantage of not allowing a permanent current to pass, and thus protects the cell to be measured.[1] As the accumulator has not a definite electromotive force, a normal element is also measured, and the readings reduced to this.

A Weston cell is used as standard; it consists of amalgamated cadmium, saturated solution of cadmium sulphate in contact with crystals of the solid salt, mercurous sulphate and mercury. Its electromotive force is 1·0186 V, and is practically independent of temperature.

The Normal Cell.—The type of an electrochemical apparatus which approaches most nearly to the theoretical conditions, is the Daniell cell (1836).

It consists of a conductor (electrode) of zinc in a solution of zinc sulphate, and one of copper in a solution of copper sulphate, the two solutions being in contact. To avoid mixing they are usually separated by a porous septum, but this is not material.

Nothing happens in the cell so long as both electrodes are not brought into metallic contact; when contact is made, an electric current passes through the conductors and the cell, as a result of which metallic copper is deposited on the copper electrode, and an equivalent quantity of zinc is dissolved at the zinc electrode. The chemical process is thus a substitution of copper in the solution by zinc. In accordance with Faraday's law, the quantity of electricity which is set in motion through the cell is proportional to the quantities of dissolved zinc and precipitated copper, being 2×96540 coul. for each mol of zinc or copper, since both metals are bivalent.

The thermal effect of the substitution of copper in the sulphate solution by zinc can be directly measured by decomposing a copper sulphate solution with zinc powder in a calorimeter. It can also be found from the tables of thermochemical data, by subtracting the heat of formation of dissolved copper sulphate from that of zinc sulphate.[2] It is $1039 - 830 = 209$ kj., or 209000 j.

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[1] The most convenient electrometer is one on the Lippmann principle. Necessary details of the technique of this and other physico-chemical measurements will be found in Ostwald-Luther's *Hand- und Hilfsbuch zur Ausführung physicochemischer Messungen*, Leipzig, 1904.

[2] As a matter of fact the heats of formation of copper compounds were determined by first determining the heats of formation of zinc compounds by dissolving the metal in acids, and then the heats of decomposition of copper salts by metallic zinc.

If we assume that the total energy which is set free in this process is changed into electrical energy, the one factor is given, viz. the quantity of electricity, 2 × 96540 coul. Dividing the quantity of energy, 209000 j., by this, the electromotive force in volts is obtained. This makes the Daniell cell 1·08 V; the observed value is 1·10 V, in good agreement with the calculated value.

Theory of the Voltaic Cell.—This agreement in the case of the best-known cell led to the belief that this was a general law. But attempts to verify this idea met with experimental difficulties.

When a cell is closed through a wire, the electrical energy is transformed into heat, which, according to Joule's law, appears in the whole circuit in proportion to the resistance at each point. In particular, a quantity of heat appears in the cell itself, the amount being to the total heat as the internal resistance of the cell is to the total resistance. If the external resistance is increased, a greater part of the heat evolution takes place outside the cell; this can easily be carried so far that the internal resistance is barely 1 per cent of the whole.

But Favre (1854) found that part of the heat cannot be taken out of the cell, since even with a very great external resistance the heat remaining in the cell did not become zero, but approached a finite limiting value, which was usually positive, but could also be negative. The latter means that more heat was taken from the cell with the current than was derived from the chemical process; this excess being taken from the surroundings. If the first phenomenon might be explained by "side reactions" which liberate heat but cannot act electrically, this would hardly meet the second case, since these side reactions would take place with absorption of heat.

This theory of the complete transformation of chemical energy into electrical energy in the voltaic cell[1] must be abandoned. The correct theory was established by W. Gibbs (1878) and Helmholtz (1882).

Since we may not assume *à priori* that in every cell the chemical energy can be transformed into electrical energy, the calculation should include the possibility of evolution of heat in the cell.

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[1] That this cannot be the case is apparent from the following considerations. Suppose a cell of the Daniell type, but with an easily fusible metal at its melting-point, and the electromotive force to be such that the chemical energy is entirely changed into electrical energy, when both metals are in the solid state. Now melt the one metal; no change of temperature is necessary for this. Suppose the electromotive force to change so that again the heat effect in the cell is zero. Now oppose the two cells; because of the difference of electromotive force, a current will be produced with which work can be done. Since the chemical process is the same in both cells, the result will be that on the one side the liquid metal dissolves, and on the other the solid will separate. But the solid metal can be melted again at the melting-point by adding heat, and so the cell be kept in action performing work for any length of time, *i.e.* at constant temperature any amount of heat can be changed into work. This would be a perpetuum mobile of the second kind, and is impossible according to the second law. Rather, both electromotive forces are equal, and if the one cell has no heat effect, the other will certainly not be the same.

Let the cell have the electromotive force π at the temperature T, and let the electrodes be n-valent, and F be the Faraday constant = 96540 coul. Imagine the quantity of electricity nF passed through the cell at T; the electrical work $nF\pi$ will be performed, and W joules will be used in keeping the temperature at T. (W may be positive or negative.) Then let the temperature be raised to $T + dT$, the electromotive force changing to $\pi + d\pi$. Under these conditions pass nF coul. through the cell in the opposite direction. We assume that the chemical process (as in the Daniell cell) is exactly reversed. Finally bring the temperature back to T; the cycle is complete, and we can use the formula that the work is to the heat absorbed, as dT to T. The work is the difference of the two electrical energies, viz. $nFd\pi$; the heat is W. The equation is $dT/T = nFd\pi/W$, or $d\pi/dT = W/nFT$. Now the heat to be added to the cell for the transformation of one mol is equal to the electrical energy taken out of the cell, $nF\pi$, less the heat given out by the chemical process, the heat of reaction R. Therefore $W = nF\pi - R$. If this be put into the above equation, $d\pi/dT = \pi/T - R/nFT$, or

$$\pi = \frac{R}{nF} + T\frac{d\pi}{dT}.$$

In this equation R/nF is the chemical energy divided by the quantity of electricity, *i.e.* the electromotive force as calculated according to the earlier views. As the formula shows, the two are not the same, except when $+ d\pi/dT$, the temperature coefficient of the electromotive force, is zero. This is approximately true in the Daniell cell, for which, therefore, $\pi = R/nF$.

In other cases, the electromotive force is not usually independent of the temperature, but varies to a very considerable extent. Changes in both directions have been observed, increase of electromotive force with rise of temperature, as well as decrease. If $d\pi/dT$ is negative, *i.e.* if the electromotive force decreases with rise of temperature, $W = nF\pi - R$ is also negative, and R is $> nF\pi$, *i.e.* the chemical energy is greater than the electrical energy. The cell must be cooled to keep its temperature constant, or it heats itself during action above the amount of Joule's heat, *i.e.* that evolved on account of the resistance. The reverse case, increase of electromotive force with rise of temperature, is connected with the fact that the cell works with absorption of heat, or cooling.

These deductions have been experimentally confirmed by many careful investigations, the latest by H. Jahn.

Cells whose electromotive force decreases with rising temperature, must pass through zero electromotive force and then change their poles. They have then become cells which take up heat and whose electromotive force increases with rise of temperature, so that this class must be considered typical for high temperatures. At the same time the term $Td\pi/dT$ becomes greater in comparison with R/nF, *i.e.* finally the chemical process plays a secondary role in the cell. There will result at last an ideal cell-state, as there is an ideal gas-state, in which the whole heat added at constant temperature is changed into electrical energy, and the heat effect due to the chemical process appears as a deviation from the ideal state.

The theory does not provide an independent calculation of electromotive force from the chemical constants for the processes in the cell, but gives the connexion between the chemical energy, the electrical energy, and a third member, which is defined by the temperature coefficient of the electromotive force. When two of these are known, the third can be calculated.

Conditions in the Normal Cell.—The next question is what must be the nature of the chemical processes in the cell, in order that the theory may be applied. The conditions are that the cell must be constant and reversible.

A cell will be constant if, during the passage of the current, the same process takes place under the same conditions. As the substances are used up during the process, they must either be present initially in sufficient quantity and concentration, or provision must be made to replace them as they are used up. But these are rather practical questions; since for theoretical purposes the current taken off may be reduced to a minimum, any cell may be held to satisfy this condition.

The real difficulty in regard to an inconstant cell is the question as to which chemical process of all those possible under the circumstances is the one which actually takes place. Thus a cell of zinc and platinum in sulphuric acid can work in several ways. So long as the kathode contains atmospheric oxygen, the hydrogen will form water at its expense. When this is used up, hydrogen will be liberated, at first dissolved in the platinum, later in the form of bubbles. A different electromotive force corresponds to each of these processes, and in order to calculate the electromotive force, the conditions under which the cell is working must be clearly defined.

A cell is reversible, if the process which takes place when the current is passed in one direction can be reversed by a current in the opposite direction. This condition is obviously very nearly fulfilled in the Daniell cell, in which this reverse reaction is possible. This condition resolves itself finally into an essentially practical one, since in general the reverse reaction is always possible. But in many instances it may be that other reactions can also take place under the same circumstances, and may quantitatively exceed the theoretical reaction. It frequently happens, too, that the immediate product of the chemical process at the electrode undergoes further changes which are difficult to reverse. In all such instances the reactions cannot be completely reversed, and sometimes apparently not at all.

Still, reversibility is often merely a question of time, and for short intervals of time is probably always present. This is shown by the fact that in using alternating currents to measure electric conductivity (p. 386), no deviations from Ohm's law have been observed, although very exact investigations have been made on this point. This proves that the energy of one current which has gone in polarising the electrodes is again made good in the next current of opposite direction, *i.e.* that the substance separated out by the first current is used again by the succeeding reversed current. Otherwise there would be a consumption of energy at the electrodes, in consequence of which there would be deviations from Ohm's law.

Ionic Reactions in the Cell.—When a current is taken from a cell, it goes not only through the external conductor, but through the cell itself. This is a combination of conductors of the first and second class. A current can pass through the first without change, but in the second it requires ions in the electrolyte as material carriers, and at the places where the electrolyte and the metal conductors, or electrodes, meet, ions must be formed from electrically neutral substances, or ions must be changed into neutral substances, for in no other way can a current pass continuously through the cell. Which of these processes occurs is indicated below. If we call the electrode at which the positive electricity enters the electrolyte the anode, the passage of the current can be effected by positive ions or kations dissolving from the anode, taking the current with them. This is what happens at the zinc of the Daniell cell. A current of positive electricity in one direction is equivalent to a negative current in the opposite direction; the same end will be attained if anions disappear instead of kations being formed. If the zinc solution of a Daniell cell is replaced by one of hydriodic acid, a positive current can enter the liquid from a metallic conductor, *e.g.* a platinum plate; the negative iodide ion of hydriodic acid is discharged and becomes ordinary iodine, which dissolves in the excess of acid. It may be considered as a neutralisation of the positive electricity on the plate by the negative electricity of the iodide ion, which then is neutral or ordinary iodine.

Similar processes occur at the kathode, *i.e.* at the electrode at which the positive current leaves the electrolyte or the negative enters it. But at it anions must go into solution or kations disappear. The latter process takes place in the Daniell cell, for there cupric ion leaves the liquid and is precipitated as metallic, *i.e.* neutral copper on the electrode. But the copper sulphate of the Daniell cell can be quite well replaced by bromine (which is dissolved in hydrobromic acid or potassium bromide solution to increase the conductivity). In this case the negative current enters the solution by the bromine taking up negative electricity and becoming bromide ion.

The essential reactions at the anode are increase of kations or decrease of anions; and at the kathode, increase of anions or decrease of kations. One of these reactions must be possible with the substances at each electrode, if a combination of conductors of the first and second class are to form a working voltaic cell. Thus there are four types of cell, viz:—

Anode.	Kathode.
Formation of kation.	Formation of anion.
Formation of kation.	Loss of kation.
Loss of anion.	Formation of anion.
Loss of anion.	Loss of kation.

Increase or decrease of the charge on existing ions is equivalent to formation or disappearance of ions (p. 401).

Examples of these types are:—

1. Zinc in zinc sulphate, bromine in hydrobromic acid.
2. Zinc in zinc sulphate, copper in copper sulphate.
3. Iodine in hydriodic acid, bromine in hydrobromic acid.
4. Iodine in hydriodic acid, copper in copper sulphate.[1]

From a chemical point of view, the processes at the anode are oxidation phenomena in the wider sense, while at the kathode the substances undergo reduction. In ordinary chemical reactions oxidation and reduction are not spatially separated, the oxidising substance being in intimate contact with the oxidisable or reducing substance, whereas they are separated in the cell.

This separation is essential for the coupling of chemical and electrical energy: because of the separate formation or disappearance of ions at the distant electrodes the electricity is compelled to pass through the circuit in the form of an electric current.

Oxidising and Reducing Agents.—Chemically considered a substance which tends to form positive ions or to use up negative ions is a reducing agent in the widest sense, while an oxidising agent strives to form negative ions or causes positive ones to disappear. The above examples afford striking proof of the correctness of this definition. At the same time it is seen that what was hitherto vaguely expressed by the terms oxidation and reduction is now completely and exactly defined.

The simple examples chosen above present no difficulty, but more complex oxidising and reducing agents are not so easy. Still it is

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[1] Since elements which form anions are scarcely known as metallic conductors, bromine and iodine must be used in conjunction with electrodes of some conducting material, which is not chemically attacked by them, while this is unnecessary with metals. There is no essential difference between them.

possible in every case to represent the matter in a similar way. The simplest case is where existing ionic charges are increased or diminished. A kation is a reducing agent when the number of charges is increased, an oxidising agent when the number is diminished. The reverse holds for anions.

Examples of the first are iron and tin, also the other metals which form kations of different valency. When ferrous ion becomes ferric ion, it acts as a reducing agent on other substances, and *vice versa.* On the other hand, if the trivalent anion ferricyanide ion increases its negative charge, passing into the quadrivalent ferrocyanide ion, it oxidises some other substance.

The more complicated cases of oxidation and reduction can all be referred to this form of increase or diminution of ionic charges. The scheme is as follows: oxidising agents (if necessary with addition of the elements of water) are formulated as hydroxyl compounds, reducing agents as hydrogen compounds, and the corresponding changes of ionic charges take place on the resulting ions. A few examples will make this clear.

Nitric acid is a strong oxidising agent, which during its action becomes NO_2 or NO. The oxidation of silver by nitric acid is usually written:

$$Ag + 2HNO_3 = AgNO_3 + H_2O + NO_2.$$

This does not represent the essential difference in the action of the two mols of nitric acid, of which only one oxidises. In accordance with the above scheme, it would be written

$$Ag + NO_2^{\cdot},OH' + H^{\cdot},NO_3' = Ag^{\cdot},NO_3' + H_2O + NO_2.$$

The kations are marked with as many dots, and the anions with as many dashes, as their valencies, and the dissociated parts are separated by a comma. The meaning of the equation is: when nitric acid acts as an oxidising agent, it is to be represented as a hydroxyl compound of the kation NO_2. Although this dissociation certainly occurs only to an extremely small extent, it is permissible to assume that if this small quantity of ion is used up in a reaction, it will be regenerated with great velocity. The oxidation consists in the $NO_2^{\cdot}$ giving its positive charge to the silver, and becoming neutral NO_2. The hydroxyl ion unites with the hydrion of the other mol of nitric acid, forming undissociated water.

The formation of NO during oxidation is to be represented in a similar manner. With addition of water, the reaction can be written

$$3Ag + NO^{\cdot\cdot\cdot},(OH)_3' + 3H^{\cdot},NO_3' = 3Ag^{\cdot},NO_3' + 3H_2O + NO.$$

The formation of a trivalent kation $NO^{\cdot\cdot\cdot}$ along with three hydroxyl ions is assumed, and the silver goes into solution as the three positive charges convert three atoms of silver into ion. The three hydroxyl ions form water with the hydrion of three mols of nitric acid, while their anions form silver nitrate with the silver ions.

To give an example of a reducing agent, we may formulate the action of sulphurous acid on iodine. Sulphurous acid as a reducing agent is to be written as a hydrogen compound of the quadrivalent anion SO_4'''', the elements of water being added, thus:

$$SO_4'''',H^{\cdot}_4 + I_2 = SO_4'',H_2^{\cdot} + 2I',H^{\cdot}.$$

The reduction of iodine to hydriodic acid is a result of the quadrivalent SO_4'''' changing to the bivalent SO_4'', the anion of sulphuric acid, the two charges going to transform two atoms of iodine into iodide ion.

This method of formulation may be regarded as a possible, but unnecessary one. But it is soon seen to be a better expression of the essential processes than the older method. This is especially evident in the case of permanganic acid. If this is written, since it is an oxidising agent, as the hydroxyl compound of septivalent manganese $HMnO_4 + 3H_2O = Mn(OH)_7$, the following relations are seen at a glance.

If permanganic acid goes into manganic acid, the hydroxyl compound of sexavalent manganese, it loses one positive unit, *i.e.* one oxidation equivalent.

If it goes into manganese peroxide (quadrivalent manganese) it yields three oxidation equivalents.

If it goes into bivalent manganous salt, it yields five oxidation equivalents.

This gives a simpler representation of the oxidising action of permanganate than the ordinary method. For the oxidation of ferrous to ferric salt, which is so much used as an analytical method, it shows at once that one mol of permanganate can oxidise five mols of ferrous ion, since each ferrous ion requires one oxidation unit, *i.e.* one ionic charge, to turn it into ferric ion.

It may still be asked what justification there is for the assumption of these multivalent ions, on which these considerations rest. Now it is quite possible to treat them from a formal standpoint, and consider these ions merely as convenient aids to calculation. Expediency is sufficient justification, but evidence can be advanced as to the real existence of these ions, although in very small amounts.[1] Just as it is in principle impossible to pump a gas completely out of a given space, it would require an infinite amount of work to completely remove a substance existing in solution from the solution. Conversely, incipient traces of every substance which are possible under the given circumstances must be formed with irresistible force. Every substance possible under the given conditions

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[1] In nitrating aromatic compounds, nitric acid acts in the sense of the dissociation $NO_2^{\cdot}$, OH'.

must be regarded as actually present. This predicts nothing as to the amounts present, and in most cases it is unknown, owing to the limitations of our analytical methods. Each improvement in this brings new confirmation of the statement; one has only to recall the endeavours of various investigators to obtain an oxygen-free space, which have led to the result that each more delicate reagent for oxygen proves it to be present, where the earlier reagents failed to indicate it, and no limit is in sight.

If all the reactions of oxidising and reducing agents are to be explained by changes in the ionic charges, the converse must hold, that all oxidising and reducing agents will, when protected from direct reaction, and provided with electrodes, give an electric current. This is fully borne out by experience; Davy in his earliest electrochemical researches (1801) prepared such cells and found them to work, and later many such combinations have been set up and investigated.

It follows from this that any chemical process, in which one substance is oxidised at the expense of another, can be arranged as a voltaic cell, and its electromotive force determined. According to p. 434, the electromotive force will not be defined by the heat effect of the chemical process, but the amount of work will be obtained which the process can perform; this may be smaller or even greater than the liberated heat-energy. In other words, this measurement gives a measure of the free energy of the reaction, and in this lies the special importance of such measurements of electromotive force.

The question naturally arises whether other chemical processes cannot be arranged to form a voltaic cell, in order that their free energy may be measured in this way. The answer is that this is generally the case if electrolytes come into the reaction. All the substances concerned do not need to be electrolytes in the ordinary sense; it is sufficient that some of them are. But other facts are required before these can be dealt with, and to these we now pass.

Concentration Cells.—If two cells are set up with zinc, zinc chloride, mercurous chloride, mercury, and opposed to each other, no current passes, since the system is symmetrical. If the zinc chloride in one cell is diluted with water, no other change being made, there is an electromotive force, proving that the system is no longer in equilibrium. If the current is allowed to flow, it acts in such a way that in the cell with the more dilute solution zinc is dissolved and mercurous chloride is decomposed, *i.e.* new zinc chloride is produced, while in the other cell zinc separates out and mercurous chloride is formed, the solution becomes poorer in zinc chloride. Equilibrium is established when the concentrations of zinc chloride in the two cells have again become equal.

The origin of the electrical energy in this cell is thus the difference in concentration of the zinc solutions, and the amount of energy obtained by the electrical method must be the same as can be obtained in any other way which equalises the concentrations.

There are several such methods. The vapour pressures of the two solutions are different, and by allowing water vapour to distil from the weak to the strong solution, the difference of pressure can be utilised to do work. If this work is calculated for the case that the excess of water to each mol of zinc chloride in the dilute solution is distilled over into the strong solution (the quantities of both solutions are assumed to be so large that neither of them materially changes in concentration during this operation), and is divided by the quantity of electricity 2F, which causes the same effect by passing between the two cells, the quotient should be the electromotive force of this concentration cell. Helmholtz (1872) showed that the calculation was in complete agreement with the observed values.

The calculation can be done in a simpler way by using the principle of osmotic pressure (Nernst, 1889). By the passage of 2F of electricity in the cell, one mol of zinc chloride is taken from the strong solution and the same amount is produced in the weak solution. The osmotic work is the same as a corresponding quantity of gas would perform if it expanded at constant temperature (as is always assumed) from the higher to the lower pressure. If p_1 and p_2 are the osmotic pressures of the two zinc chloride solutions, and i the total number of mols which result from the ionisation of one mol of zinc chloride, this work is given by $iRT \lg (p_1/p_2)$. The quantity of electricity which has been passed through the double cell is 2F, the electromotive force π is

$$\pi = \frac{iRT}{2F} \cdot \lg \frac{p_1}{p_2}.$$

In the case of dilute solutions $i = 3$, since $ZnCl_2$ gives three ions.

The formula is identical with the one obtained from consideration of the vapour pressure of the solutions. This is obtained by using the relation between vapour pressure and osmotic pressure developed on p. 182. The development may be left to the reader.

The formula may be generalised by substituting the general value n for the particular number 2. It contains only the concentrations of the two salt solutions, and holds for all similar cases where two cells of this kind are opposed to each other. The zinc can be replaced by any other metal which permits of the preparation of an electrode and of an electrolytic solution, and not only can the mercurous chloride be replaced by other sparingly soluble mercurous salts, but even this metal and its salt may be replaced by any other metal and its sparingly soluble salts, without altering the fundamental considerations in the least. Since the constants R and F are independent of the nature of the substances, the electromotive force is independent of the nature of the substances, if the factors i and n are the same, and if these are different, the electromotive forces are in a simple ratio.

All these conclusions (Ostwald, 1892) have been satisfactorily established by experiment (Goodwin, 1893).

For numerical calculation the following data are necessary. The constant R in absolute units is $8{\cdot}31 \times 10^7$; F is 96540 coul. Dividing by ·4343 to convert natural logarithms into decadic logarithms and remembering that 1 volt × 1 coul = 10^7 erg., the factor becomes

$$\frac{8{\cdot}31\mathrm{T}}{{\cdot}4343 \times 96540} = {\cdot}0001982\mathrm{T},$$

for which ·0002 T can be substituted with an error of 1 per cent. For room temperature, 18° C = 291° A, we have

$$\pi = {\cdot}0577\frac{\mathrm{i}}{\mathrm{n}} \cdot \log\frac{\mathrm{p}_1}{\mathrm{p}_2} \text{ Volt.}$$

In the above case of zinc chloride, for dilute solutions i = 3, and n = 2; with a concentration ratio 1 : 10, whose logarithm = 1, the electromotive force will be ·075 V. A very great difference of concentration will not give a specially high electromotive force, since this only increases as the logarithm of the ratio of the osmotic pressures or concentrations, therefore much slower than the ratio itself.

Concentration Cells with Migration.—It might be thought that the arrangement described above of two opposed cells could be replaced by a simpler cell, made up of two zinc electrodes, each in a zinc salt solution of different concentration. Such simple concentration cells do give an electromotive force in the same direction as the other cell, but it is always smaller. This is because the change of concentration which is produced by the passage of the current is not so great as corresponds to the current according to Faraday's law; and this was assumed to take place in the development of the formula. The change of concentration is less, since migration comes in question (p. 389). The passage of nF electricity does not change the concentration by one mol, but by v/(u + v) of a mol, u being the velocity of migration of the kation, and v that of the anion. The work is in the same ratio, and the electromotive force so much smaller; the formula being

$$\pi = \frac{2\mathrm{v}}{\mathrm{u}+\mathrm{v}} \cdot \frac{\mathrm{i}}{\mathrm{n}} \cdot {\cdot}0002\mathrm{T} \log\frac{\mathrm{p}_1}{\mathrm{p}_2}.$$

Osmotic Theory of the Cell.—If we consider that similar considerations are applicable not only to the equalisation of two concentrations of a salt, but to changes of concentration of any substance concerned in the production of the current, we see that the same line of thought, the calculation of the osmotic work done by the passage of the current through the cell, leads to a theory of the voltaic cell. This has been accomplished to a considerable extent (van't Hoff, 1885; Nernst, 1889) by taking account of the osmotic work in the electrolytic solution of metals. A solid substance behaves to a liquid in the same way as a volatile substance does to a vapour space. According to the concentration of the solution the solid will either go into solution, or solid will be precipitated on it from the solution, until equilibrium is attained, *i.e.* until a definite concentration, the saturation concentration, has been established.

If this is not already present, work can be performed by the process of saturation. If the solution is unsaturated, the work is gained by the dissolution of the solid; if it is supersaturated, it is gained by the concentration of the solution becoming smaller, and separation of the solid.

This work can be calculated in the case of a volatile substance whose vapour follows the gas laws. If p_0 is the saturation pressure and p the initial pressure, each mol of vapour at constant temperature T can perform the work $RT \lg (p_0/p)$ in passing from p_0 to p.

The same formula holds for solutions, p being now osmotic pressure.

It must be observed that it is not necessary, for the validity of this formula, that the vapour should have the same composition as the other phase. A solid substance which yields gaseous decomposition products follows precisely the same laws, all that is necessary is the reversibility of the transformation. This is true also for solutions; it does not matter what becomes of the solid on going into solution, so long as it can be recovered from it.

Metals which can form ions are cases of this kind. The zinc ion in the solution of a zinc salt is undoubtedly different from a mere solution of metallic zinc; it can be formed from metallic zinc, and be reconverted into it, so that its formation in solution from the metal (apart from the electrical work which will be taken into account immediately) must be regarded as associated with the same amount of work as in a case of ordinary solution. Similarly the solution of a salt follows the same law (if due regard is paid to the increased number of mols) although we know that it, too, is changed into something else, *i.e.* its ions.

But a new circumstance arises in the passage of a metal into its ion. We know from the phenomena of electrolytic conduction that quantities of electricity move with the ions and are combined with them. If the electric charges are removed, their ionic character is lost, and they become neutral substances. No electrical phenomena are observed when a salt goes into solution, although it is bound up with formation of ions, because positive and negative ions are formed in equivalent amounts. External electrical effects are impossible under these circumstances. But when a metal goes into solution as ion, it can only form kations or positively charged ions; for this a corresponding quantity of positive electricity must be added, or negative electricity subtracted.

The solution of metals is therefore well adapted for the production of electrical phenomena. Since ion formation cannot take place without the latter, the electrical and chemical processes can be united, and we thus have machines for converting chemical energy into electrical energy, and *vice versa.*

In the Daniell cell, considered from this point of view, a definite solution pressure is ascribed to the zinc, which expresses its tendency to form zinc ion. If this pressure is greater than the osmotic pressure of zinc ion in the solution, the transition from metal to the solution corresponds to the possibility of an output of work. Since this transition can only take place simultaneously with a movement of electricity, this work can be obtained entirely in the form of electrical energy.

But for this it is necessary to fulfil the condition that there shall be no excess of electricity in the interior of the conductor. The positive electricity which enters the solution with zinc ion, must be removed from the solution in some similar manner. In the Daniell cell, this is effected by the separation from the solution of an equivalent quantity of cupric ion. Since this occurs at two different places, at the zinc and copper electrodes, the process cannot begin until the two electrodes are connected together and the movement of electricity rendered possible.

Further, the separation of cupric ion from the solution cannot take place without gain or loss of work: and this is to be calculated exactly as for zinc, except that the sign is changed, since instead of the entrance of zinc ion, we have cupric ion leaving the solution. The electromotive force of the cell is thus the difference of the two values at the electrodes.

If the solution pressures of zinc and copper are denoted by P_1 and P_2, and the osmotic pressures of zinc ion and cupric ion in the solutions by p_1 and p_2, the total work which can be taken from the cell if 1 mol of zinc is dissolved, and 1 mol of copper is precipitated, is given by the difference $RT \lg (P_1/p_1) - RT \lg (P_2/p_2)$.

The osmotic pressures of the ions are easily calculated from the concentrations and the degrees of ionisation. We have no starting-point for the measurement of the solution pressures of the metals; P_1 and P_2 must be regarded as fixed but unknown. They depend on the nature of the metal, on the temperature, and on the solvent. But, as we are immediately concerned with aqueous solutions, this last may be left out of account. If we work at constant temperature there remains one variable only, the nature of the metal.

To express the work gained by electrochemical processes in measurable units, we have to remember that electrical energy is the product of quantity of electricity and electromotive force. The former is given by Faraday's law and is n × 96540 coul. = nF, n being the valency of the ion which results from 1 mol of the metal. By division of the work by the quantity of electricity we obtain the electromotive force at the electrode. It is

$$\pi = \frac{RT}{nF} \lg \frac{P}{p}.$$

A cell consists of two electrodes in their solutions connected together in the opposite direction, *i.e.* metal/electrolyte—electrolyte/metal. The electromotive force of the cell is thus the difference of the two potentials at the electrodes. The potentials between the two electrolytes and between the two metals are to be taken into account; we shall see later that the former is always very small, and the latter probably zero or very nearly so. They may both be provisionally neglected.

The electromotive force of the cell is given by an equation of the form

$$\pi = \pi_1 - \pi_2 = \frac{RT}{F}\left(\frac{1}{n_1} \lg \frac{P_1}{p_1} - \frac{1}{n_2} \lg \frac{P_2}{p_2}\right).$$

The symbols marked 1 and 2 relate to the two electrodes and their solutions. R/F has already been found to be ·000198, if Brigg's logarithms are used instead of natural logarithms. The equation becomes

$$\pi = \cdot 000198T\left(\frac{1}{n_1} \log \frac{P_1}{p_1} - \frac{1}{n_2} \log \frac{P_2}{p_2}\right).$$

If $n_1 = n_2$, the expression simplifies to

$$\pi = \frac{\cdot 000198T}{n} \log \frac{P_1}{P_2} \cdot \frac{p_2}{p_1}.$$

Anode and Kathode.—The changes of potential which arise when the values of p are altered, cannot be conveniently denoted by the terms positive and negative. From the times of Volta's theory, which erroneously regarded the origin of the electromotive force in a cell to be the contact of the two metals, it has remained the custom to denote the zinc as the positive and the copper as the negative metal. But in the Daniell cell the zinc is negative when the copper is brought to zero potential (by connecting it to earth), and the copper is positive if the zinc is connected to earth. An unambiguous nomenclature is based on Faraday's names for the electrodes. A kathode is the electrode at which kations are discharged from the solution, an anode the one at which anions are discharged. The definition is extended to include formation of anions as equivalent to separation of kations as a criterion of the kathode, and at an anode, kations may be sent into solution, this being equivalent to the separation of anions from the solution (which seldom occurs).

An electrode becomes more anodic when the tendency of the anions to leave the liquid, or of the kations to enter it, increases. Similarly an electrode becomes more kathodic when the tendency of the kations to pass from the liquid to the electrode is greater, or the tendency of the anions to do the same becomes smaller. A cell has a greater electromotive force, the more kathodic the one electrode is, and the more anodic the other is.

If an electrode becomes more kathodic, the positive potential on the electrode increases, if it is reckoned from the potential of the liquid; conversely, the negative potential of the liquid becomes greater (or the positive becomes smaller), if the electrode is taken as the starting-point. The contrary holds for an electrode which becomes more anodic.

In the Daniell cell zinc is the anode, copper the kathode. If the concentration of zinc ion is increased, the tendency of zinc to form ions is diminished, owing to the increased osmotic pressure. The zinc anode becomes less anodic and the total electromotive force falls. Increase of concentration of copper salt at the kathode increases the tendency of cupric ion to deposit on the electrode. The kathode becomes more kathodic and the electromotive force of the cell increases. This is quite general, and the following rule holds: increase of concentration of the ions of the metal in the electrolyte (the kations) makes the metal in it more kathodic or less anodic.

These definitions agree with the formula for the electromotive force in a cell, if the potentials are counted from the anode.

Single Potentials.—Many conclusions can be drawn from the formula for single potentials. Since the values of the solution pressures are unknown, we are limited to cases in which they are constant and hence disappear.

In the equation for the potential of an electrode

$$\pi = \frac{0{\cdot}000198\mathrm{T}}{n} \log \frac{\mathrm{P}}{p},$$

the anion does not occur. The conclusion is that the potential is independent of it, and will have the same value in all salts of the same metal at equivalent concentration, provided the degree of ionisation is the same.

This has been fully established. With twenty-one different thallium salts (1/50 normal), and mercury in mercurous chloride and potassium chloride as the other half of the cell, the following electromotive forces were obtained (Neumann, 1894):—

Anion.	Volt.	Anion.	Volt.
Hydroxide	·7040	Succinate	·7040
Fluoride	·7050	Tartrate	·7050
Carbonate	·7050	Citrate	·7055
Sulphate	·7050	Fumarate	·7040
Nitrate	·7055	Maleate	·7060
Formate	·7045	Itaconate	·7050
Acetate	·7055	Citraconate	·7050
Butyrate	·7046	Benzoate	·7050
Monochloracetate	·7050	Salicylate	·7055
Propionate	·7045	Phthalate	·7055
Malonate	·7050		

It has also been shown that the electromotive force of the Daniell cell remains the same when the sulphate solutions are replaced by equivalent solutions with other anions. The conclusion that dilution of the salt at the anode increases the electromotive force of the cell, and dilution of the kathode solution decreases it, has also been experimentally verified by the Daniell cell. If both solutions are diluted or concentrated in the same ratio, the electromotive force remains unchanged. This is a consequence of the fact that both metals have the same valency ($n_1 = n_2$ in the formula).

Sparingly Soluble Electrolytes.—The electromotive force cannot be altered to any great extent by altering the concentration. If a 10 normal solution be the strongest possible, for a bivalent metal like zinc or copper, dilution to a ·001 normal solution—the most dilute which can be used with any certainty—only changes the electromotive force by less than 0·12 V. But there are other means by which the concentration of kations can be reduced to very small amounts. The two most important are to employ sparingly soluble salts of the metal, or electrolytes in which the metal forms complex compounds.

The first case we have already made use of in the mercury-mercurous chloride electrode. An electrode of mercury covered with mercurous chloride, and the solution of a chloride added as electrolyte, behaves just as a metal in a solution of its salt, *i.e.* is unpolarisable (for weak currents). If a positive current passes from the mercury into the liquid, more mercurous chloride is formed; with the reverse current, mercury increases at the expense of the mercurous chloride; in each case without any change of potential. In the first case chloride ion disappears from the solution, in the second it enters into solution, and the system behaves as if it was an electrode of metallic chlorine, which can take up and give out chloride ion. Further, the concentration of chloride ion in the solution has an effect on the potential: if it is increased, the electrode becomes more anodic.

This can be foreseen if we make use of the general idea that all substances are soluble. The mercurous chloride goes into solution until its solubility product is reached, and the potential depends on the concentration of mercurous ion. Since increasing the concentration of chloride ion diminishes that of the mercurous ion according to the law of mass-action, the electrode will become less kathodic.

Numerically the effect is the same as if the electrode sent out univalent chloride ion. The equation for the dissolved mercurous chloride is, if the mercury is assumed to be univalent,[1] $a \times b =$ constant, a being the concentration of chloride ion, b of mercurous ion. The osmotic pressures of the two ions are inversely proportional to each other, and denoting them by p and p_1, $\log p = -\log p_1 + c$, where c is a constant. If this is put into the equation for an electrode, $\pi = \frac{\cdot 000198T}{n} \log Pp_1$, and the osmotic pressure of chloride ion affects the potential to the same extent as mercurous ion does, but in the opposite direction.

Precipitation reactions can be measured electrochemically in cells with sparingly soluble salts, and their free energy determined in this way. Consider a cell made up of silver in silver nitrate, and silver in potassium chloride and silver chloride, a solution of potassium nitrate being interposed to prevent direct precipitation. This cell has an electromotive force of ·51 V, the silver chloride side being anode. If the current is allowed to pass through the cell, at the anode silver becomes silver chloride, while metallic silver separates at the kathode. At the same time, potassium ion migrates to the kathode, and nitrate ion in the opposite direction; they form potassium nitrate in the middle vessel. The only result is, since the quantity of silver which unites with chlorine on the one side is equal to the quantity separated at the other, the diminution of the concentration of silver nitrate and potassium chloride with formation of silver chloride and potassium nitrate, *i.e.* just as if silver nitrate and potassium chloride had been brought into direct contact.

Any precipitation reaction can be dealt with in the same way, provided that the metal of the precipitate can be employed as an electrode.[2]

A further conclusion may be drawn from the observed electromotive force of ·51 V. Since the cell is a concentration cell with the same metal as both electrodes, $P_1 = P_2$, and since $n = 1$, the equation becomes $\cdot 51 = \cdot 000198T \log \frac{p_1}{p_2}$. The only unknown is p_2, since the silver nitrate solution was 1/10 normal. If the pressure p_1 be put $= \cdot 1$ (the unit does not matter, since we have in the formula the ratio of two pressures), we have, since $\cdot 000198T = \cdot 0576$,

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[1] In concentrated solutions the mercurous ion must be represented, partially at least, as bivalent $Hg_2^{\cdot\cdot}$. This has no effect in the present instance, since the valency of the kation falls out of the final equation.

[2] There are special devices which get rid of this limitation, viz. electrodes of the "third kind" (Luther, 1898).

$\log p_2 = -9{\cdot}85$, *i.e.* $p_2 = 1{\cdot}4 \times 10^{-10}$. This is the solubility of silver chloride in the 1n potassium chloride. To find the solubility l, in pure water, we use the law of the constancy of the product of the two ionic concentrations, $l^2 = 1 \times 1{\cdot}4 \times 10^{-10}$, whence $l = 1{\cdot}2 \times 10^{-5}$. The solubility of silver chloride was found by the conductivity method (p. 409) to be $1{\cdot}06 \times 10^{-5}$ mols in 1 litre.

The solubility of sparingly soluble salts can generally be found in the same way. Smaller solubilities can be measured by this process than by any other, since the electromotive force increases as the logarithm of the dilution; and in fact there is no limit to the method. Finite values are found in all cases (Goodwin, 1894), a proof that there is no really insoluble salt. For such would give infinitely great electromotive force, as may be seen from the equation when $p_2 = 0$.

Complex Electrolytes.—A second method of reducing the concentration of metal ion in an electrolyte is to apply a reagent which converts the ion into a complex compound. As the osmotic pressure acting against the solution of metal in the cell is exercised only by its own ion, and not by any other compound which may contain it, it is possible for solutions which contain large amounts of the metal to give potentials which correspond to extremely small ionic concentrations.

These phenomena are most strikingly shown by cells in which potassium cyanide is an electrolyte. Alkali cyanide forms complex compounds with very many heavy metals, which are present as a constituent of the anion. Potassium ferrocyanide and ferricyanide, potassium silver cyanide, potassium gold cyanide, the platinocyanides, etc., may be cited as examples. Observations on the migration phenomena have proved that in all these compounds the heavy metal does not migrate to the kathode but to the anode during electrolysis; it is therefore a constituent of the anion. The complex ammonia derivatives of cobalt, platinum, copper and silver are similar, except that the metal migrates to the kathode, as it is part of a complex kation. Still their complex nature is shown by the fact that they do not give the usual reactions of the metal ions.

The abnormal solubility of sparingly soluble salts in a reagent is generally satisfactory evidence of the formation of complex compounds. When silver chloride dissolves in ammonia, it can only be that one of the ions of silver chloride has disappeared from the solution. As this is excluded so far as chloride ion is concerned, it must be the silver ion, and equilibrium thus leads to the conclusion that silver ion is present only in very small amount in ammonia solutions of silver salts.

The concentration of metallic ion in solution can only be affected in one way by the formation of complexes, that is, diminution. Such substances always make a metal more anodic, never more kathodic. This was empirically known long before the theory of it.

The alteration is often very great; Jacobi (1845) observed that the poles were reversed in a cell with silver in strong solution of potassium cyanide and zinc in zinc sulphate; zinc was kathode and silver anode. If the circuit is closed, metallic zinc is displaced by the silver which goes into solution.

The concentration of metal ion in the complex solution can be calculated from the electromotive force of a cell comprising such an electrode and one of the same metal in a solution of an ordinary salt. The calculation is exactly the same as for the solubility of an "insoluble" salt (p. 448). The results show that though the concentration may be extraordinarily small, it never becomes zero, for the electromotive force, large as it is in some instances, does not become infinitely great, as it should if the concentration became zero.

For example, a ·1n potassium cyanide solution, which contained ·01 mol silver, against a ·01n normal silver nitrate solution, gave 1·14 V, whence the concentration of silver ion is 2×10^{-18} mol in a litre.

Combining these results with those on p. 448, we are led to the following conclusion. The formation of an "insoluble" salt displaces the potential to the anode side, corresponding to its solubility. Such a salt dissolves under certain circumstances in a reagent, in which the metallic ion goes into a complex compound. For this to occur, the concentration of ion in the complex solution must be smaller than in a saturated solution of the sparingly soluble salt. The potential must also be more anodic than in the presence of the "insoluble" salt; and thus the potentials must stand in direct relationship to the solubilities.

Thus, all silver salts, except the sulphide, dissolve in potassium cyanide solution; their solutions must contain more silver ion than the silver cyanide solution, and the corresponding electrode must be less anodic.

Silver chloride and bromide dissolve in sodium thiosulphate, but silver iodide scarcely does so; silver chloride dissolves in ammonia, bromide and iodide scarcely at all. The concentration of silver ion must increase in the following order: sulphide, cyanide, iodide, thiosulphate, bromide, ammonia compound, chloride. The electromotive force against a silver electrode in silver nitrate must decrease in the same order, as is shown by the following measurements.

Silver nitrate (·1n)—	Sodium sulphide		1·36 V
	Silver iodide	in potassium cyanide	1·31 „
	„	in potassium iodide	·91 „
	Silver bromide	in sodium thiosulphate	·84 „
	„	in potassium bromide	·64 „
	Silver chloride	in ammonia	·54 „
	„	in potassium chloride	·51 „

The solutions were normal and contained a little silver.

It is apparent from these measurements that the chemical process of forming complex ions can be utilised for the production of electrical energy, and also that the chemical potential of these reactions can be determined electrometrically. After this treatment of the changes of concentration effected by simple dilution and by the precipitation of "insoluble" salts, there now remain only oxidation and reduction as possible ionic reactions to complete the thesis that any ionic reaction can be utilised for the production of an electrical potential.

Gas Cells.—The cells to be now considered are also concentration cells. Still they present certain peculiarities which demand separate treatment.

As stated on a previous occasion, the terms oxidation and reduction have been extended to include processes which are traditionally in this category, although oxygen or hydrogen have nothing to do with them directly. It was shown there that increase of positive or decrease of negative charges must be regarded as the essential characteristic of a substance which is oxidised, and increase of negative or decrease of positive charges for oxidising substances. As free electricity cannot exist in a solution, such a change cannot occur without the opposite change on some other substance, *i.e.* no oxidation can take place without a simultaneous reduction, and conversely. A process of this kind can always be imagined in the reverse direction. A substance which has served as a reducing agent by having taken up positive charges, is now in a position to act as an oxidising agent by giving up these positive charges to another substance. An equilibrium will in general result between the substances which change their charges; these may eventually suffer other chemical changes, after the original substances have so far diminished in concentration, and the resulting substances increased so far, that the two opposing reactions balance each other.

For this process to be electrically active, the substances must be kept apart, and it must be possible for the electric charges which correspond to the conditions to equalise themselves. In the above cells with electrodes whose metals took part in the chemical reactions, both these functions were fulfilled by the metals. The zinc of the Daniell cell provides not only zinc ion, but also for the conduction of the necessary positive charges. If the chemical process takes place between substances which are in solution, a special electrode must be introduced whose sole function is to conduct the electricity. Such a metal should not react to any marked extent with the electrolyte. Platinum is chiefly used, but other metals may be used according to the nature of the reaction at the electrode, or even other conductors of the first class.

A very simple cell of this kind consists of any acid as electrolyte, and two platinum plates charged with hydrogen. If both plates are equally charged with gas the arrangement is symmetrical, and there is no electromotive force, but if the pressures of hydrogen on the two sides are unequal, an electromotive force will result. The current will tend to equalise the difference of pressure; the gas will disappear at the place of greater pressure, and gas will be formed at the other place. In other words, the hydrogen under the greater pressure will be the anode.

A cell of this kind may be regarded as a concentration cell with electrodes of metallic hydrogen. The solution pressure will vary directly as the gas pressure, while the osmotic pressure of hydrion in the electrolyte is the same on both sides. The tendency of the hydrogen to ionise must be greater at the electrode with the more concentrated hydrogen, *i.e.* the more strongly compressed hydrogen is anodic to the other.

The arrangement in this cell is different from the previous concentration cells, in which the osmotic pressure varied, and the solution pressure of the electrode metal was constant. Here the former is constant and the solution pressure varies. Ordinary cells of this type can be constructed by using amalgams in place of pure metals as electrodes. If two amalgams of different concentration are placed in the same electrolyte and are connected together, an electromotive force is obtained, the richer amalgam losing metal and the other gaining it. The former is therefore anode and the latter kathode, just as in the hydrogen cell.

The electromotive force can be calculated, if the work is taken into account, equally well for the gaseous hydrogen as for the dissolved hydrogen, on the assumption that the electrodes contain a store of gas at the pressures obtaining on each side.

If 1 mol hydrogen under the pressure q_1 disappears, the same amount appears at the other side under the smaller pressure q_2, and the work which can be isothermally obtained is RT lg (q_1/q_2). The quantity of electricity, since the gas has the formula H_2 (*i.e.* the work RT refers to 2·02 g. hydrogen), is 2F, and the electromotive force

$$\pi = \frac{RT}{2F} \lg \frac{q_1}{q_2}.$$

To apply the osmotic theory to this cell, attention must be paid to a point which did not arise before. If a metal electrode goes into ion the work which is available is to be placed to the account of the ions, since the volume change of the metal is negligibly small. It is different if the transformation takes place in substances which are dissolved in the electrolyte. If these become ions the osmotic work due to their disappearance must be taken account of, just as in the production of ions. The two are not, as a rule, equivalent, since the number of mols changes during the transformation. Thus one mol of hydrogen H_2 gives two mols of hydrion $H^{\cdot}$, one mol of oxygen in conjunction with water gives four mols of hydroxidion:

$$O_2 + 2H_2O = 4OH'.$$

To formulate the process in such a cell we have m_1 mols of neutral substance disappearing at the anode, and n_1 mols of ion formed: at the kathode m_2 mols disappear, and n_2 mols of ion are formed. The quantity of electricity which passes through the cell is sF, s is the product of the numbers n and the valency of the ions concerned. The equation then is,

$$\pi = C + \frac{RT}{sF}(m_1 \lg P_1 - n_1 \lg p_1 - m_2 \lg P_2 + n_2 \lg p_2)$$

or

$$\pi = C + \frac{RT}{sF}\left(\lg \frac{P_1^{m_1}}{p_1^{n_1}} - \lg \frac{P_2^{m_2}}{p_2^{n_2}}\right),$$

where P_1 and P_2 are the osmotic pressures of the neutral substances, p_1 and p_2 of the kations[1]; C is a constant which is a function of the temperature and of the chemical nature of the substances.

The proof of this formula is based on the same principles as the simpler formula on p. 452, but as its development turns on minute details, it may be omitted here. The value of C will be obtained immediately from a simple point of view.

If this formula is applied to the foregoing cell the osmotic pressures of hydrion are equal, $p_1 = p_2$. The osmotic pressures of the dissolved neutral hydrogen is, according to Henry's law, proportional to the gas pressure; P_1/P_2 is thus equal to q_1/q_2. To obtain C, make the gas pressures equal; the cell becomes symmetrical, and $\pi = 0$. At the same time the logarithmic term becomes 1, the logarithm therefore 0, and $C = 0$. Since C does not depend on the concentration, this is its value for cells with different pressures. Finally $s = 2$, $m_1 = m_2 = 1$, $n_1 = n_2 = 2$; on substituting these in the equation we get $\pi = \frac{RT}{2F} \lg \frac{q_1}{q_2}$, the earlier equation.

The same result is obtained as was obtained before on the basis of direct considerations with practically no calculations. The fuller formula is not superfluous, as we shall soon come to cases where the simpler method fails and the general formula has to be used.

Hitherto the above relations have not been tested experimentally in this simple form. Grove, the discoverer of gas cells (1839), noticed that a cell with nitrogen on one side and hydrogen on the other gave an electromotive force and a current, in which hydrogen was the anode. Since nitrogen has been proved to take no part in producing a current, this was a hydrogen cell, the partial pressure of hydrogen on the nitrogen side being very small.

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[1] If p_1 or p_2 relate to anions, the ± sign must be reversed owing to the reversed sign of the potentials.

The arrangement of such cells is shown in Fig. 64. The platinum electrodes should be covered with platinum black; they then absorb much more gas and the cells are more constant. The active part of the gas is that on the electrode.

A concentration cell of the usual type is obtained by having two hydrogen electrodes of the same pressure in two electrolytes of different hydrion concentration. The electrode will be more anodic the more dilute the solution of hydrion is, and their potentials will be the same when the hydrion concentrations are equal, whatever anion be present. All these conclusions have been satisfactorily confirmed (Smale, 1894).

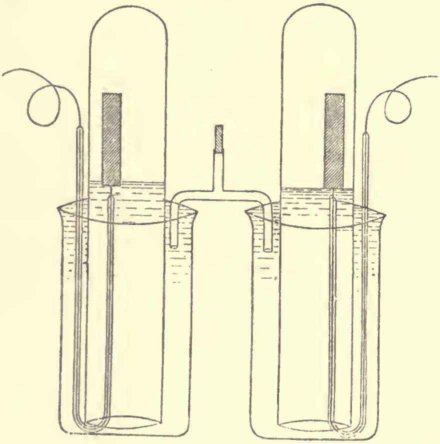

FIG. 64.

The same considerations apply in the case of an oxygen electrode. The simplest view taken of a platinum electrode saturated with oxygen gas is that it can form hydroxidion. Hydroxyl solutions, *i.e.* alkaline liquids are the appropriate electrolytes. The possibilities need not be repeated, they are the same as for hydrogen electrodes. The only difference is that 1 mol of oxygen, O_2, with water gives 4 mols of hydroxidion, OH′, and gives four negative units, so that in the equation $n = 4$; the sign of the potential is also reversed.

The Neutralisation Cell.—There is a particular cell which engaged the attention of Becquerel long ago (1823). It consists of two hydrogen or oxygen electrodes at equal pressure, the one in acid the other in alkali. The electrolytes are separated by an indifferent liquid, *e.g.* the neutral salt. The electromotive force is considerable, reaching ·76 V for normal solutions. The same voltage is obtained whether the electrodes are oxygen or hydrogen. The alkali electrode is always the anode.

We will consider the hydrogen electrode, after which the oxygen electrode will present no difficulty. At first sight hydrogen in alkali should have an infinitely large potential, since hydroxidion is present in large excess, so that hydrion might be thought to be entirely absent, having combined with hydroxidion to form water. But if we consider that increase of hydroxidion in the solution can diminish hydrion, but never make it entirely disappear, the result is obvious.

The two concentrations are connected by the equation $ho = kc$, h and o being the concentrations of hydrion and hydroxidion, c that of water. The latter is constant; consequently the product ho must be constant in all aqueous solutions.[1]

We have therefore a concentration cell, in which the hydrion concentration on the alkali side is reduced to a very small amount by the presence of hydroxidion, whence the electromotive force is fairly large.

The electromotive force obviously depends on the dissociation constant of water; and k can, conversely, be calculated from it. It is carried out exactly as on p. 454, for in the formula

$$\pi = \frac{RT}{nF} \lg \frac{P_1 p_2}{P_2 p_1},$$

since $P_1 = P_2$, and for hydrion, whose concentration alone is concerned, $n = 1$,

$$\pi = \frac{RT}{F} \lg \frac{p_2}{p_1} = \cdot 0577 \log \frac{p_2}{p_1}.$$

Remembering that the potential at the contact of an acid and a base is ·065 V (Nernst, 1894) we obtain for the concentration of hydrion in normal alkali $\cdot 6 \times 10^{-14}$. The product ho has the same value, and, denoting the concentration of hydrion and hydroxidion in pure water by a, $a^2 = ho = \cdot 6 \times 10^{-14}$, whence $a = \cdot 8 \times 10^{-7}$, *i.e.* 1 mol $H^{\cdot}$ and OH' in about 10,000,000 litres. The dissociation constant of water was first obtained by Ostwald (1893) in this way; the result agrees well with the values obtained in other ways (*e.g.* conductivity, p. 404).

The same applies to the corresponding oxygen cell. The solution pressures disappear as the gas pressures are the same, and the circumstance that 1 mol oxygen gives rise to 4 mols of hydroxidion has no special influence.

If the process in this cell is more closely looked into, it is seen to be an electromotive application of the process of neutralisation. Consider the hydrogen cell again, and let 2F be sent through it. One mol hydrogen disappears at the anode, and the same amount is evolved at the kathode; no gas has been used up. At the same time one mol of water has been formed at the anode, the hydrion sent out from the electrode uniting with hydroxidion. At the kathode the same amount of hydrion has disappeared to become gas. The kation on the basic side, and the anion on the acid side have migrated towards each other, and have formed the mixture which we call the

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[1] Strictly, c is not the same in all solutions, but decreases as foreign substances are dissolved in the water. The vapour pressure is the measure of the active mass of water, and it is diminished by dissolving other substances in it. But for normal solutions of an electrolyte the decrease is only 2 or 3 per cent, and may be neglected here.

neutral salt of the two constituents. The content of base and acid has decreased by two equivalents, and the corresponding amount of neutral salt has been formed, while the gas has played the role of intermediary and has gained or lost no work. The cell is thus essentially a neutralisation or salt-forming cell.

The earlier measurements of the acid-alkali cell were made before the presence of gases was known to be necessary. But by working with platinum electrodes in air there is always enough free oxygen on the electrodes to give the right conditions, for the first few moments at least.

The Oxygen-Hydrogen Cell.—The oxygen-hydrogen cell has been longest known of all the gas cells. It consists of the two gases in conjunction with any electrolyte. It gives a constant electromotive force of 1·06 V at 17° C and atmospheric pressure, and is independent of the nature or concentration of the (dilute) electrolyte. The potentials at the electrodes may differ considerably, but the sum is constant. If the cell is closed, both gases disappear with formation of hydrion and hydroxidion at the electrodes. If the electrolyte is an acid, it increases at the anode, and diminishes at the kathode; with a basic liquid the converse holds. If the electrolyte is neutral, it becomes acid at the anode, basic at the kathode.

This shows that we have here the simplest type of an oxidation and reduction cell (p. 451), for the reducing agent is completely changed to hydrion, and the oxidising agent to hydroxidion.

The exact behaviour of the cell is realised when the general formula of p. 453 is applied. In

$$\pi = C + \frac{RT}{sF}\left(\lg \frac{P_1^{m_1}}{p_1^{n_1}} - \lg \frac{P_2^{m_2}}{p_2^{n_2}}\right)$$

$s = 4$, $m_1 = 2$, $n_1 = 4$, $m_2 = 1$, $n_2 = 4$; P_1 and P_2 are constant for given values of temperature and pressure; the sign of the second term of the equation is +, since oxygen forms an anion. Further, from the dissociation equation for water $p_1 p_2 = \text{constant}$. When these are substituted in the equation, the whole expression within the brackets becomes constant, and with it the electromotive force, provided dilute aqueous solutions are used as the electrolyte.

If the pressure of the two gases is changed, π changes too, being larger with increased pressure of either gas. But they are not affected to the same extent, the effect on hydrogen being double that on oxygen. All these results of the equation have been confirmed by experiment (Smale, 1894).

Oxidation and Reduction Cells.—These considerations give also the general theory of oxidation and reduction cells, composed of two unattackable electrodes and an oxidising and a reducing agent. For reducing agents in general can be represented as substances which tend to form hydrion, and oxidising agents those which tend to form hydroxidion; and as these tendencies in the gases vary with the pressure, any oxidising agent may be imagined to be replaced by oxygen under the appropriate pressure. The same holds for hydrogen and reducing agents. The pressures, indeed, soon become impossible, for the electrical potential increases as the logarithm of the pressure, which therefore will have to increase in geometrical ratio if the potential increases in arithmetical ratio. But theoretically the above equation can be applied to all cells whose electrodes consist of reducing and oxidising agents of any kind.

The equation also shows that the electromotive effect of these substances depends on the osmotic pressure of the ions which are formed in the process. The potential of a ferrous salt as a reducing agent will be affected by the concentration of ferric ion in the solution; increase of it will cause a fall in the anode potential and a weakening of the cell. Any means which will reduce the concentration of ferric ion, will increase the potential. Fluorides are such agents. The fluorides of trivalent metals are very slightly ionised; addition of potassium fluoride to an iron solution causes the disappearance of the greater part of the ferric ion, and the anode potential to rise. This effect is easily observed; moderate additions of apparently indifferent substances may raise the potential of such an electrode to the extent of ·7 V (Peters, 1898).

A generalisation from these relations is obvious. Any reducing agent will show a stronger reducing action in alkaline solution, because the opposing hydrion concentration is smallest in alkaline solution. Conversely acid reaction strengthens the oxidising action of an oxidising agent. If the chemical reaction is the same in acid and in alkaline solution, the difference is already known: it is m × ·76 (p. 454) where m is the change of concentration of $H^{\cdot}$ for 1F according to the chemical equation (Luther, 1899); the differences actually observed are smaller than this. From this it appears that the transformations of hydrogen and oxygen into their ions are the only reactions which do not essentially change in any way by the change from acid to alkaline reaction.

Practical Importance.—Cells of this kind are particularly interesting because they hold out the promise of a better utilisation of chemical energy for technical purposes than has ever been attained in the steam engine. The heat of combustion of "knall-gas" is 286 kj.; this divided by 2F gives 1·48 V, the electromotive force of the gas cell if the chemical energy is completely transformed into electrical energy. The actual value is 1·06 V; 72 per cent of the heat is utilised, whereas the steam engine seldom gives more than 15 per cent. The ratio would be similar if other combustible material such as coal or the easily prepared generator gas could be substituted for hydrogen. The technical realisation of this idea has failed hitherto, because the chemical processes in these cells proceed so slowly at ordinary temperature that the dimensions of an apparatus to yield moderate quantities of energy would be enormous. There are two ways out of the difficulty. Suitable catalytic accelerators may be discovered which will make the velocity of the process sufficiently great at ordinary temperature. Or, as the velocity is increased by raising the temperature, a cell might be constructed to work at higher temperatures. If this is once reached, it would be kept hot by the Joule's heat in the cell, and, of course, the more easily the larger the installation.

Up to the present the experiments made to overcome the difficulty have gone in both these directions, although sometimes unintentionally so. The success achieved so far leaves us no room to imagine that a developable form has been found.

Volta's Theory of the Cell.—Volta had attempted to resolve the electromotive force at the terminals of his pile into the single potentials, and was led by his experiments, which we now know were erroneous, to the following representation. In the series—copper, zinc, moist conductor, copper—which shows an electromotive force between the end plates, the first copper being negative, the latter positive, the chief part of the potential is between the two metals, since copper in contact with zinc is negative, the latter metal therefore positive.[1] There are potentials between the metals and the moist conductor, but they are small, and in particular become zero when water or neutral salts are employed.

The fact that the electrometer gives no indication, when the two metals are simply placed in contact, was explained by Volta on the basis of his law of series of potential. It runs that the potential between two metals remains the same when any number of metals are interposed. In other words, the sum of the potentials at the contacts of any series of metals is the same as that between the end metals of the series in direct contact. Since the parts of an electrometer which give the indication consist of metallic parts of the same material the potential between these parts (*e.g.* two gold leaves) will, according to this law, be zero however many metals in any order whatsoever are connected with them, and the electrometer will give no indication.

But if a moist conductor is introduced between two different metals, there are no potentials at these points, and the electrometer will show the potential difference of the metals.

Suppose the cell to contain, for example, zinc and gold and to be connected by gold wires with a gold leaf electrometer. According to Volta there is a potential at the contact between the zinc and gold, this is counterbalanced by the potential at the contact in reverse order. This holds if any other metal is inserted.

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[1] From this copper used to be called the negative metal and zinc the positive metal.

If a moist conductor is laid between gold and zinc at one of the contacts, conduction will take place without the introduction of any new potential in the circuit. The electrometer shows a positive swing on the side where the gold leaf is in metallic connexion with the zinc.

This representation gives a formally satisfactory account of potentials, but it can give no answer to the question which arose half a century later as to the source of electrical energy. This could be proved to be undoubtedly the chemical process, which could occur between metal and moist conductor, but not between metal and metal.

In a dim fashion this contradiction was known to the contemporaries of Volta, and Ritter's discovery (1798) that the potential series of metals in Volta's sense is the same as the series of oxidisability, or chemical affinity for oxygen, gave the "chemical theory" of the cell a definite foundation.

As a matter of fact, the same results are obtained on the converse assumption, *i.e.* that there is no potential at the contacts of metals, but only at the contacts with moist conductors. Any series of metals gives, then, no potential, and the electrometer remains unaffected when connected with a purely metallic series. If a moist conductor is introduced, there result at the two contacts of the metals with it two potentials whose difference acts on the electrometer. According to this view the zinc is negative to the moist conductor and the copper positive. Only those metals affect the potential which are in immediate contact with the moist conductor, since potentials can only arise here. The other metals in the circuit have no effect at all.

Both theories can explain the same series of facts (especially if air is considered a moist conductor, although of very small conductivity). This circumstance, that each isolated fact could be explained in both ways, was the cause of the long contest between the contact theory and the chemical theory of the voltaic cell.

Single Potentials.—Mercury.—The close connexion between chemical and electrical energy is now recognised, and it is clear that the electrical energy, manifested as electromotive force, can only arise in chemical processes. There is thus very great probability that the potentials also are located at the contacts of metal and electrolyte. Still it is always possible to save the contact theory by artificial *ad hoc* assumptions. Independent proof of the potentials would be of great significance.

The cause of this uncertainty is that even the simplest cell has three different points of contact, and potential differences may arise at any or all of them. Other cells can be constructed with the same substances, but all attempts to calculate any single potential from measurements made on all possible arrangements of a definite number of substances fail, for there is always one equation too few; an arbitrary value can therefore be assigned to any one potential without contradiction. The struggle between the two theories lasted so long, because each of them had to make one assumption, and it was impossible to formally prove either assumption to be wrong.

The problem, then, was to find a datum regarding one of the potentials in some other independent manner. At present there is one single independent process, and this settles the question in favour of the chemical theory. A second process is highly desirable to eliminate as far as possible errors in interpretation of the results of the first process, but no one has yet been successful in finding one free from objections.

This process depends on the following facts. A drop of mercury under an electrolyte has a definite surface-tension which changes when the electrical potential between the liquid and the mercury is changed. The surface-tension of mercury in sulphuric acid decreases when anodically polarised; this cannot be carried far, because electrolysis soon begins, and the mercury becomes coated with mercurous sulphate. If the mercury is kathodically polarised the surface-tension gradually increases, reaches a maximum at about ·9 V and then again decreases. Bubbles of hydrogen gas, due to decomposition of sulphuric acid, do not begin to come off until the surface-tension has decreased to a moderate extent.

To change the potential between mercury and sulphuric acid in a manner adapted to measurement, a very large and a very small mercury surface are placed in contact with the sulphuric acid. If a definite electrical potential is applied to the two masses of mercury, it is divided between the two in inverse ratio of the surfaces, and the change practically affects only the small surface.

Since in general the mercury-sulphuric acid interface is the seat of an electrical potential difference, electrical energy is accumulated there, just as on the two coatings of a Leyden-jar, between which a potential difference has been established. This energy acts as a kind of surface energy, the surface tending to change, and according to electrostatics, it strives to extend, since this is connected with a decrease of potential. The electric charge acts against the surface-tension, which strives to reduce the surface, and the observed surface-tension is the difference of the two effects.

The following behaviour is a direct consequence of what has been already said. If the surface-tension is determined for any given electrical potential at the interface, any alteration in the latter which increases the surface-tension must consist in a reduction of the difference of electrical potential in the surface. If the alteration is carried still further in the same direction, the electrical charge will finally become zero. At this point the surface-tension has its highest value, for if the electrical condition is altered still further in the same direction, a charge is again produced. Although it now has the different sign, it still retains the property of reducing the surface-tension which must again begin to diminish. This is confirmed by experiment, hence the conclusion: the difference of electrical potential at the interface is zero when the surface-tension has its greatest value.

Since this condition results when a potential difference of ·9 V is applied to mercury in sulphuric acid (saturated with mercurous sulphate),[1] the conclusion is arrived at that the potential difference which is spontaneously established between mercury and sulphuric acid has this value with the opposite sign. Since the applied potential was kathodic, the liquid is made more positive when the difference is compensated; therefore under natural conditions the mercury is ·9 V more positive than the liquid.

Other Metals.—The potential between mercury and any other electrolyte can be determined in the same manner. The electrolyte must have a definite concentration of mercurous ion if the potential is to be accurately defined; since most mercurous salts are sparingly soluble, the saturated solution of the particular salt is suitably employed.

If such a mercury electrode is connected with another metal in its electrolyte, the two liquids being in contact, a cell is formed whose electromotive force can be measured. Subtraction of the known value for the mercury electrode gives the potential between the metal and the electrolyte. This gives a method of determining all other single potentials.

Two assumptions are here made, that the potential between the two electrolytes, and that between the two metals are either zero or very small. The former can be calculated in certain cases (Nernst, 1889; Planck, 1890) from considerations, the principles of which are well understood, and it is always possible to so arrange the experiment that the calculation can be made. It is found that in many instances these potentials do not exceed ·01 V, and can easily be reduced to still smaller amounts.

There are substantial grounds for the belief that the potentials between metals are very small, if not quite zero. It is justifiable, therefore, to neglect both of these potentials, and to consider the electromotive force of the cell as the sum of the two potentials at the electrodes.

Normal Electrode.—A "normal electrode," which is easily reproducible, is used in the determination of single potentials. It consists of mercury with mercurous chloride in normal solution of potassium chloride saturated with mercurous chloride. Apart from the fact that the potential difference between the metal and the electrolyte is known (as explained above), measurements of potential of any single

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[1] The value varies to some extent with the concentration of the sulphuric acid.

electrode can be made in terms of such a normal electrode; the results are better defined than the previous usual measurements of the total electromotive force of a cell.

The construction of a normal electrode is shown in Fig. 65. The rubber tube, closed by a spring clip, is filled with the potassium chloride solution, and allows the electrode to be conveniently connected with the other electrode. The potential between mercury and the solution is 0·56 V; the mercury is positive to the liquid, and the liquid is negative to the metal.

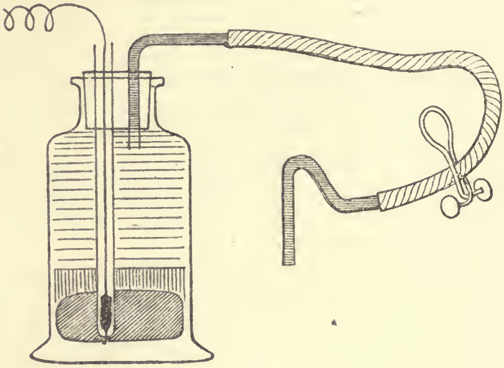

Fig. 65.

The Potential Series of Metals.—The potential between a metal and its electrolyte is dependent on the concentration of its ion in the electrolyte, as appears from the formula on p. 445. In the following table the solutions are normal: the ionic concentration is smaller than this, about ·6 to ·8 normal, because of incomplete ionisation. The sign gives the potential of the electrolyte, if that of the metal is put as zero.

Magnesium	+1·24
Aluminium	1·03
Manganese	·82
Zinc	·51
Cadmium	·16
Thallium	·11
Iron	·09
Cobalt	– ·02
Nickel	·02
Tin *	·09
Lead	·10
Hydrogen	– ·25
Antimony *	·38
Bismuth *	·50
Arsenic *	·55
Copper	·59
Mercury	1·03
Silver	1·06
Palladium	1·07
Platinum *	1·14
Gold *	1·36

The values for the metals marked with an asterisk are approximate, as solutions cannot be prepared of known ionic concentration.

We see in this table the old potential series of Volta, Ritter and Berzelius, only in a more definite form. The significance of the above potentials is that they are a measure of the chemical affinity of the metals, or their tendency to form ions, *i.e.* to form salts. Any metal with a greater positive value displaces those with smaller potential from their salts, itself going into the ionic state.

At the same time this series only holds for comparable ionic concentrations. The ratios are different in electrolytes which form complex compounds of the metal, as is evident from the abnormal potentials of the metal in these circumstances (p. 450). If the ionic concentrations are known from other experiments, *e.g.* from solubility determinations (p. 409) the chemical behaviour of the metals can be predicted.

Comparison of these potentials with the table of heats of formation of the ions (p. 277) is interesting. The two series are in the same direction, but are by no means proportional to each other. The chemical energy is by no means completely converted into electrical energy in the process of ionisation; the differences are in both directions. If these differences did not exist, cells with metal electrodes would be independent of temperature (p. 434) which is not found to be the case.[1]

The Potential Series of Oxidising and Reducing Agents.—A potential series of oxidising and reducing agents may be appended to the series of metals; they are obtained in the same way as the metal potentials. They refer to the reagents as usually prepared. Since there is no definite concentration of the product of reaction present, the conditions are not accurately definite; still they will give a general idea of the values. The sign is the same as in the previous table, it indicates the potential of the liquid when the metal potential is put as zero.

Stannous chloride in alkali	+ ·30
Sodium sulphide	·09
Hydroxylamine in alkali	·06
Chromous acetate in alkali	·03
Pyrogallol in alkali	– ·08
Hydroquinone in alkali	·23
Hydrogen	·25
Zinc hydrosulphite	·28
Potassium ferrous oxalate	·29
Potassium ferrrocyanide in alkali	·48
Iodine in alkali	·49
Stannous chloride, acid	·50
Potassium arsenite	·51
Cuprous chloride	·56
Sodium thiosulphate	·58
Sodium sulphite	·58
Potassium ferrocyanide	·59
Ferrous sulphate, neutral	·63
Hydroxylamine, acid	·64
Sodium bisulphite	– ·66
Sulphurous acid	·72
Ferrous sulphate, acid	·78
Potassium ferric oxalate	·85
Iodine in potassium iodide	·89
Potassium ferricyanide	·98
Potassium bichromate	1·06
Potassium nitrite	1·14
Chlorine in alkali	1·19
Ferric chloride	1·24
Nitric acid	1·26
Bromine in alkali	1·32
Chromic acid	1·40
Chloric acid	1·42
Bromine in potassium bromide	1·43
Potassium iodate	1·49
Manganese peroxide	1·63
Chlorine in acid	1·67
Potassium permanganate	1·76

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[1] The determination of the heat of ionisation is based on measurement of the heat effect at the electrodes during the formation or transformation of ions. These are affected by the heat effects due to the differences of electrical potential; knowledge of this gives the possibility of calculating the heats of ionisation.

CHAPTER XIX

ELECTROLYSIS AND POLARISATION

General.—When an electric current enters or leaves an electrolyte, a chemical process, which primarily consists of the formation of ions from neutral substances, or the conversion of ions into neutral substances, or a change in the number of ionic charges, necessarily takes place at the electrode. There may be other secondary processes which will vary with the nature of the substances employed and with the circumstances of each case.

This primary process is necessary, because electricity can only move in an electrolyte in conjunction with ions, while outside it, it is independent of ions. At the boundary surface there must be a process which consists in the transference of electric charges.

These processes are not primarily dependent on the nature of the conductor which forms the boundary of the electrolyte. In particular, metallic electrodes are not a necessity, for Davy showed that the chemical process at the boundary did not cease when a current passed from the electrolyte into air (by means of a brush discharge).

The process is known as electrolysis. Both changes of energy and of material have to be taken into consideration.

Deposition of Metal.—The simplest material change is that which occurs when the ions which have brought the electricity to the electrodes lose their charges and pass into the neutral state without changing in composition. This is frequently the case with salts of heavy metals, which deposit metal at the kathode. The metal is generally coherent, so that the process finds extended application in reproducing objects in metal, and in depositing a metal covering on objects, processes known as galvanoplastics and electroplating.

For these arts it is of importance to obtain the metal in a smooth, coherent form. This is effected by mechanical means, the surface being made as smooth and as even as possible to begin with, and inequalities prevented during deposition by mechanical polishing. If an inequality is once formed, it affords a shorter passage for the current between it and the anode, and will continue to grow in consequence of the increased deposition of metal there.

There are also chemical influences, for small alterations of the bath often entirely change the character of the deposit. The reasons for this are only partially known. Frequently it is the simultaneous separation of non-metallic products of electrolysis (gases, oxides, etc.) which cause bad deposits; additions to the bath which prevent this will improve the deposit. There is also the hitherto unexplained fact that deposition from complex salts, in which the concentration of the metal ion is very small, generally gives a much smoother covering than do ordinary salts. Gold and silver are examples.

Mixed Solutions.—If several metals are present in a solution they will be deposited in the order given by the table on p. 462. Those whose anodic nature, or tendency to form ions, is small will come out first, and the others will follow in the order of their tendency. The potential of a metal to its solution varies with the concentration of its ion, but as a diminution of the latter to 1/1000, which is the limit of most analytical methods, only makes a difference of ·08 V in the case of a bivalent metal, it is evident that two metals can be separated whose potentials in equally strong solutions do not differ by more than about ·1 V.

The order is changed if the metals are in complex solutions, for the metal is more anodic the more dilute the metal ion is in the complex solution. The analogous complex solutions of different metals are often very different in this respect, resulting in certain circumstances in considerable divergences from the usual position of the metals. For example, zinc forms with alkali cyanides a fairly unstable complex, copper, on the other hand, an exceedingly stable one. Both metals are displaced to the anodic side, copper much more so than zinc; as a result both lie close together, and on electrolysis they are deposited at the same time (as brass).

On comparing the metals in the series given on p. 462 we find hydrogen between lead and antimony: we must expect that the latter, but not lead, can separate out from aqueous solution. But we know that not only lead, but cadmium and zinc can be deposited, although the potential of the latter metal is about ·76 V more anodic than hydrogen.

It may be said that the potential of hydrogen is measured in a normal acid solution and that in neutral solution it would be displaced about ·4 V to the anode side. Cadmium would then come before it, but zinc would be about ·3 V after it. The cause is that the given value for hydrogen only holds for equilibrium. If on electrolysis hydrogen separates out, very considerable supersaturation occurs, and a corresponding rise of potential is necessary to produce bubbles of gas. Hence the possibility of the electrical deposition of zinc. To avoid the dangerous vicinity of the hydrogen potential the zinc solution must be neutral and as strong as possible. Further, the deposition will proceed better if the precipitate is smooth so as not to facilitate the first formation of bubbles. As a rule, the "super-potential" (or over-voltage) attainable will depend on the nature of the metal of the kathode, and on the condition of its surface.

Metals which are still more anodic will not be separated at all. The alkali metals can be obtained, it is true, when mercury or some other liquid metal is used as the electrode. The potential of the metal dissolved in mercury is less anodic than the pure metal, since it is there in solution, and can only be obtained from it by the expenditure of work. Also, the surface of a liquid metal presents the maximum of smoothness attainable, and gives rise to a specially large over-voltage, with the result that the potentials necessary for the separation of these metals can be applied before hydrogen gas is evolved.

These processes are technically made use of in the manufacture of the alkali metals, and of their hydroxides (by the action of water on the amalgams).

The ions of the halogens, which go into the free elements when discharged, behave in a similar manner. Here, too, the ions of water come in; while iodine and bromine present no peculiarities, it is a question of concentration whether chlorine or oxygen will appear: and with fluorine there is no question, for only oxygen can be obtained. This is because the discharge of hydroxidion from the water, in spite of its very slight concentration in the solution of hydrofluoric acid, occurs at a smaller potential than that of fluoride ion, and accordingly only oxygen is liberated. The discharge of chloride ion from hydrochloric acid occurs more readily the greater the concentration of chloride ion and the smaller that of hydroxidion in the solution. Both these are fulfilled in concentrated hydrochloric acid, the large concentration of hydrion depressing the concentration of hydroxidion. The more dilute the acid, the more oxygen is liberated in the electrolysis.

Conduction and Discharge.—One important point in the above consideration will be repeatedly noticed afterwards, viz. the important part in the results of an electrolysis taken by ions which are present in very small concentration. As a general rule the various ions contribute to the transport of the electricity in proportion to their concentrations and migration velocities; their discharge at the electrode, on the contrary, depends on their potential with respect to the neutral form. If the concentration of an ion is small, but has a small discharge potential, the small quantity present will begin to discharge. The concentration falls, the potential rises, and unless much of the substance is present, a new ion must soon begin to discharge. The case is different if the concentration of the ion is small, but can be renewed as fast as it is used up.

This can happen in two ways. The ion may be a component of a sparingly soluble salt, which continues to dissolve as the ion is removed from solution. Or, and this is a more frequent and more important way, another compound may be present in equilibrium with the ion, and supply fresh amounts of the ion as it is removed from solution. This occurs when a complex compound is present, the equilibrium between it and the ion being such that a large concentration of the compound corresponds to a small concentration of the ion.

An example of this is the silver cyanide ion of the complex potassium silver cyanide, $KAg(CN)_2$, which is dissociated to a small extent in the manner represented by the equation, $Ag(CN)_2' = Ag^{\cdot} + 2CN'$. In spite of the exceedingly small concentration of silver ion in this solution (p. 450), a beautiful silver deposit is formed on the kathode even with moderately large currents; as the small amount of silver ion is discharged, more is formed according to the above reaction, and the liquid practically behaves as if all the silver were present as ion. The same holds for hydrion and hydroxidion in aqueous solutions.

This behaviour is therefore always possible, if the corresponding reaction is possible. It depends on the velocity of the reaction whether it will take place in any given case. Ionic reactions are extremely rapid, but not infinitely so, and certain phenomena indicate that the velocities are measurably different.

Transformation of Ions at the Electrodes.—Partial discharge or charge of the ions may occur at the electrodes in place of complete discharge, if the intermediate substances are capable of existence, *i.e.* a change of valency can occur. Thus at the anode ferrous ion becomes ferric ion, and ferric ion becomes ferrous ion at the kathode. Similar changes are obviously possible with all other metals which form ions of different valencies. Compound anions can also undergo the same change if they can exist with different valencies, as the trivalent and quadrivalent ion $Fe(CN)_6$, and others.

These ionic changes are more striking if there is simultaneously a change of molar weight. The ion of sulphuric acid SO_4'' loses at the anode one charge, and at the same time two partially discharged ions condense to the ion of persulphuric acid S_2O_8''. The ion of carbonic acid behaves similarly. So, too, the thiosulphate ion S_2O_3'' loses one negative charge and changes into tetrathionate ion, S_4O_6''.

The limiting case is reached in those processes in which the discharged ion cannot form a neutral substance of the same composition. Decomposition generally takes place, frequently with interaction of water. Thus the discharged kation, NH_4, of ammonium salts decomposes at the kathode into ammonia and hydrogen,

$2NH_4 = 2NH_3 + H_2$; acetate ion, CH_3CO_2, decomposes into ethane and carbon dioxide, $2CH_3CO_2 = C_2H_6 + 2CO_2$. The discharged anions of the inorganic oxygen acids react with water of the solution regenerating the acid with liberation of oxygen; if they can form a compound with more oxygen, they are converted into these, *e.g.* discharged chlorate ion into perchloric acid,

$$2ClO_3 + H_2O = HClO_3 + HClO_4.$$

Finally, the participation of the substances present in the solution may constitute the principal reaction, and the electrolysis is analogous to cells worked by oxidising and reducing agents. The substances at the anode are oxidised, those at the kathode reduced, as is apparent if the definitions on p. 438 are applied. This region, which includes the electrolytic treatment of organic substances, has afforded many new methods of preparation, which have the advantage that the oxidation or reduction can be affected without introducing foreign substances. A further advantage is that the products of the reaction can be varied in numerous ways by simply altering the potential, which can be done by employing acid or alkaline solution, etc. In particular it has been found that the nature of the electrodes has often a very marked catalytic effect on the products which result. The velocity with which the changes of concentration at the electrodes are equalised also influences the course of the reaction to a large degree.

Primary and Secondary Processes.—It is frequently asked which of the reactions at the electrodes are primary and which are secondary. If the question is not directly answered by the composition of the ions and of the products, there is usually some doubt as to which of the possible reactions actually occurs. For instance, when an aqueous solution of sodium sulphate is electrolysed, oxygen appears at the anode and the anode liquid becomes acid, while at the kathode hydrogen is liberated and the liquid becomes alkaline. Formerly it was supposed that the salt was split up into acid and base, and the water into its elements. This assumption is contrary to Faraday's law, and Hittorf demonstrated that the current is conducted by the ions $2Na^{\cdot}$ and SO_4'' in the ratio of their migration velocities. But the discharged anion cannot exist as a neutral substance; it passes into sulphuric acid and oxygen. In this sense the oxygen is a secondary product. The hydrogen at the kathode may also be regarded as secondary, on the assumption that sodium first appears and immediately acts upon the water to form sodium hydroxide with evolution of hydrogen. If we reflect, however, that in sodium hydroxide solution we have only sodium ion and hydroxidion, this assumption means that sodium ion is discharged to be immediately changed back to sodium ion. It is simpler to assume that the sodium ion is not discharged at all, the hydrion of the water taking its place. Although the concentration of the latter ion is small, it is regenerated from the water, so that there is always sufficient present to be discharged. The residual hydroxidion gives the alkaline reaction.

If a mercury electrode is used, sodium is actually liberated, and dissolves in the mercury. On the one hand the kathode potential at a mercury electrode can be raised much more than at any other electrode (p. 466); on the other, the anodic potential of sodium dissolved in mercury is much smaller than for that of pure metal. It can be made very small by largely increasing the dilution (p. 452); consequently a certain quantity of sodium will be taken up by the mercury before the evolution of hydrogen at a mercury surface is reached. In this case sodium is a primary product; after it has reached a certain concentration in the mercury, hydrogen will appear as the primary product in place of sodium.

The various problems that present themselves can be dealt with in a similar manner. There is still one point of importance to be mentioned. The potential at the electrode is not conditioned by the mean concentration of the substances in the mass of liquid, but entirely by the concentration in the immediate vicinity of the electrode. When they are changed during electrolysis, it depends on mechanical conditions, such as diffusion, convection, stirring, and the like, what are the concentrations at any moment in contact with the electrode. A similar influence is exerted by the different velocities with which the reactions take place. Although the rule may be laid down that at any given moment that ion will be discharged at the electrode, whose discharge potential is the smallest, it is often difficult to say under the circumstances which of the ions present at that moment possesses this property.

Polarisation Potential.—The second question regarding the phenomena of electrolysis concerns the work which is necessary for the separation of the different substances. It is to be noticed, first of all, that the work is the sum of two terms, which relate to the two electrodes, and can be made to a large degree independent of each other. The development of our knowledge of these phenomena has been greatly hindered by the circumstance that in most of the investigations the sum of the processes at the two electrodes was alone considered, without any attempt to resolve it into its components.

The work which is expended or gained in electrolytic transformations is expressed by the potential, just as in the case of the voltaic cell, since the quantity of electricity is governed by Faraday's law independently of the potentials. If π is the potential in volts, n the valency of the discharged ion, $96540\ \pi\ n$ is the work in joules, which is required for the separation of one mol of the ion.

The decomposition potential of an ion is the same as the potential which the same substance (as electrode or at the electrode) gives rise to in a voltaic cell (Le Blanc, 1893). It is assumed that the concentrations of the substances concerned are the same, and also that the reaction is reversible. The latter is apparently always the case in rapid processes; if there are slow secondary reactions at the electrode, the velocity of reformation of the ion from the ultimate products of electrolysis may be so small that the cell cannot be regarded as practically reversible. Such cases are excluded.

When the product of electrolysis is a solid, a metal for instance, the law is easily tested. The difficulties are greater with gaseous products, especially with hydrogen and oxygen.

While the potentials of solids depend only on the ionic concentration in the electrolyte, the latter vary widely, owing to supersaturation phenomena. The complicated systems which these form long delayed the recognition of the simple behaviour of the typical systems, because they were more frequently investigated under the erroneous idea that they were typical. In spite of this, it has been shown that a continuous current can be sent through an acid or an alkali with the same potential as, or a very slightly higher one than, that of the oxygen-hydrogen cell (p. 456), *i.e.* 1·06 V. Still in this very case there are unexplained circumstances, which cannot be entered into here.

Unpolarisable Electrodes.—This is the name given to certain combinations of metals and their solutions, which have the property that no polarisation or opposing potential ensues when a current is sent through them. In a strict sense there is no unpolarisable electrode, since the concentration of the solution is changed at the electrodes by the passage of the current (except in the cases in which the two ions have exactly the same migration velocity), and a change of potential is the inevitable consequence. But there are different degrees of polarisation, and for a metal in a solution of its salt the system is more easily polarised to a given extent, *i.e.* by a smaller current, the more dilute the metal ion is. The quantity of metal deposited is proportional to the current strength, but not the change of potential, which alters by equal amounts when the concentration alters in equal ratios. If a given current has separated two-thirds of the metal present, and created a certain polarisation in doing so, one-third of that current will now suffice to bring about the same change, and after that only one-ninth of the original current is required to produce the same effect.

The solution must necessarily contain the metal in some form if an electrode is to be unpolarisable, although it is not necessarily present as ion. For in such cases as the silver cyanide compounds, where the ion concentration is very small, a silver electrode is very slightly polarisable, since the silver ion used up at the electrode is immediately replaced by dissociation of the complex. The potential at the electrode, of course, is affected by it.

A system made up of two equal unpolarisable electrodes with an electrolyte interposed acts as a metallic conductor when a current is passed through it, for the potential at the one electrode is exactly balanced by the opposed potential at the other electrode. Before the use of alternating currents was discovered, this was practically the only way of measuring the resistance of electrolytes.

Polarisation at the interface of two electrolytes is always inconsiderable, in accordance with the circumstance that the potential between liquids is always small. Any number of liquids can be brought into circuit without polarisation, if they are interposed between the liquids of two equal unpolarisable electrodes.

Accumulators.—The energy stored up in polarised electrodes is obtained again if the electrodes are connected with a conductor, the chemical process being reversed. A system of this kind is an electrical accumulator. It has been already mentioned that any electrolytic process is theoretically reversible, at least if the recombination takes place very soon after electrolysis, and if the electrodes are not overcharged, *i.e.* caused to discharge products which are removed from the conducting surfaces, and are thus removed from the reaction.

This is not sufficient for practical purposes, where an accumulator must retain its energy unchanged as long as possible, and must store up in the electrodes the largest possible quantities of energy. Although any voltaic cell, in which the chemical process can be reversed by sending a current through it in the reverse direction (*e.g.* a Daniell cell) can act as an accumulator, the above practical conditions limit the choice, so that up to the present only one type has survived. That is the lead accumulator.

It consists of two electrodes of lead, in as porous a condition as possible, in dilute sulphuric acid. One of them is previously treated as anode in sulphuric acid, and the lead in it converted into lead peroxide (see under). When the cell is closed, sulphate ion migrates to the plate of metallic lead, hydrion to the peroxide plate. At the former lead sulphate is formed according to the equation $Pb + SO_4 = PbSO_4$, the discharged SO_4 uniting with lead. At the other electrode the peroxide is reduced by the discharged hydrogen to oxide which forms lead sulphate with the sulphuric acid. The chemical result of the passage of the current is lead sulphate. A considerable quantity of energy is liberated, since the electromotive force is about 2 V.

If a current is sent in the opposite direction through the accumulator after it is discharged, *i.e.* after lead sulphate has been formed at both plates, the sulphate at the kathode is again reduced to metallic lead, hydrogen displacing lead with formation of sulphuric acid. The sulphate ion travels to the anode, is there discharged, and reacts with lead sulphate and water in the following manner:

$$PbSO_4 + SO_4 + 2H_2O = PbO_2 + 2H_2SO_4.$$

Lead peroxide and sulphuric acid are regenerated, and the accumulator is in its original condition.

The accumulator has particular advantages, owing to the happy circumstance that the same metal can be used for both electrodes, and that all the compounds concerned in it, with the exception of sulphuric acid, are sparingly soluble. In the first place, the reacting substances cannot diffuse away from the electrodes (as the copper sulphate does, for example, in the Daniell cell); then the formation of "local currents" is impossible, since they are due to particles of the kathode metal settling on the anode, and there producing a short-circuited cell, which leads to a useless consumption of the anode. Thus two important factors which cause waste of the stored-up energy are excluded. The large electrochemical equivalent of lead is a serious drawback, as it limits the amount of energy per unit weight of electrode.

In use the accumulator has been found to yield at most about 90 per cent of the energy. The loss is mainly due to the change of concentration of the sulphuric acid on the passage of the current. A glance at the equations representing the chemical processes shows that when the accumulator is working sulphuric acid is used at both electrodes, *i.e.* goes out of the solution into the electrodes; during charging up, the acid is again set free. During work the sulphuric acid at the electrodes becomes dilute, and in consequence the potential sinks, as closer consideration will show. The potential during discharge can only be maintained in proportion as the sulphuric acid is renewed by diffusion and convection.

Conversely, the sulphuric acid at the electrodes becomes more concentrated during charging, and this leads to an increase of potential above its usual value, which makes a correspondingly higher energy necessary for charging.

It follows from this that the loss during discharge and the increased potential required during charging will be greater the stronger the current is, because the equalisation of concentration will be less complete. It is found to be true that, within certain limits, the accumulator works more economically the smaller the current strength per unit of electrode surface.

In addition to this source of loss, there is also the resistance of the cell, and the corresponding transformation of electrical energy into heat. It is made as small as possible by arranging the electrodes in the form of plates, which gives a large extension of surface, and putting them close together, so that the acid layer between them is as thin as possible. The internal resistance of good accumulators is very small, and in most cases need hardly be taken into account.

BOOK V

MICROCHEMISTRY

CHAPTER XX

THEORY

General.—The various divisions of general chemistry are based on the different kinds of energy which, in conjunction with chemical energy, make up the properties and behaviour of substances. While heat, volume energy, and electrical energy have long been represented by thermochemistry, chemical mechanics, and electrochemistry, the significance of surface energy has only recently been recognised, and this at first only in isolated, apparently unconnected cases, such as adsorption, suspensions, colloids, etc. But later the view has gained ground that these are but the different chapters of a connected whole, which is characterised by the phenomena of surface energy. As this energy only assumes measurable proportions when at least one dimension of the system has a microscopic value, and only comes into play in a layer of about 10^{-7} cm. in thickness, the division may be called microchemistry.[1]

Microchemical effects occur in all chemical investigations and measurements, for an object to be investigated must be confined within boundaries. But these, represented by the surface between different phases, or at least between the homogeneous object under investigation and the walls of the containing vessel, are the seat of surface energies, which exert a direct and definite influence on the condition of the whole system. As a rule the effect is so small in comparison with that of the other forms of energy, that it is far below the errors of observation and measurement. But when the ratio of the surface to the total amount of the system becomes relatively large, the effects of surface energy, which are proportional

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[1] The name "capillary chemistry," which first suggests itself, is unsuitable on linguistic grounds.

to the extension of the surface, become of some account. For this reason a large number of very exact quantitative laws have been discovered, without taking into account the surface energy, although it was never absent. The surface energy of the quantities of substances usually handled under ordinary conditions is vanishingly small. The first question then is to find out under what conditions surface energy begins to produce recognisable effects.

Specific Surface.—If the "internal energy," *i.e.* the total energy with the exception of the surface energy, be represented by I, and the surface energy by O, the total energy of a system is $I + O$. The former is proportional to the volume v, the other is proportional to the surface w. If we put $I = iv$ and $O = gw$, i being the internal energy of unit volume and g the surface tension, the total energy is $iv + gw$ and the total energy of unit volume is $i + gw/v$. In ordinary measurements the first term i alone is taken into account, for g is so small that the second term disappears unless the quotient w/v becomes large. The surface tension of water, which has a greater surface tension than any other liquid, at 0° is only 77 in absolute units. The formation of the 6 sq. cm. surface of a cm. cube with volume of 1 ccm. requires the expenditure of $6 \times 77 = 462$ erg. This is equivalent to $1{\cdot}1 \times 10^{-5}$ cal., which would warm one gram of water a little over ·00001°. This gives some idea of the influence exerted by surface energy on the properties of this amount of water, provided that it retains its cubical shape. If it is divided into smaller cubes the quantity remains the same, but the surface increases in inverse ratio to the side of the cube. When the side of the cube approaches the limit of visibility at about 10^{-5} cm., the energy required for the surface formation corresponds to 1·1 cal. or a corresponding change in the water. This effect is not inconsiderable, as the vapour pressure changes about 8 per cent for this difference of temperature.

The essential difference is that for equal volumes the surface can have different values, from a minimum when the form is spherical to an unlimited high value when the form is different. The specific surface (Wolfg. Ostwald, 1905), which is the surface divided by the volume, is a convenient expression of this effect. If l is the side of a cube, its surface is $6l^2$ and its volume l^3, its specific surface is therefore $6/l$. A cube with 6 cm. side has unit specific surface. A similar calculation for the sphere shows that a sphere of 3 cm. radius has unit specific volume; thus a cube and the inscribed sphere have the same specific surface.

As the above calculation leads us to expect, surface energy effects do not attain much importance until the specific surface is greater than 10,000.

Values of this order can result from the diminution of one, two, or all three dimensions. In the first case we have films, bubbles, and the like, in the second threads, and in the last fine powders and drops. A cube cut with shears into thin parallel plates gives the first kind, a second division normal to the first will give rise to threads, and a third series of sections normal to the other two will yield cubes or rectangular parallelopipeds. If n is the number of sections, the new surface in the first case will be 2n as great as the original surface; in the second and third instances it will be 4n and 6n times as large as at first. A large specific surface is obtained when one dimension at least becomes very small; diminution of the other dimensions only increases the effect twofold and threefold. If a body is to have marked surface energy, one dimension at least must be less than 1/1000 mm., *i.e.* approximate to the limit of microscopic visibility (about $1{\cdot}5 \times 10^{-5}$).

Theory of Surface Phenomena.—In the simplest case of a pure liquid (or solid) in contact with its vapour, it was shown (p. 80) that the interface differs from the interior of either phase, and possesses a special kind of energy, which is proportional to the size of the interface, and to a coefficient, *i.e.* the surface tension. The former is the capacity factor, the latter the intensity factor of this energy. Unlike the volume energy of a gas which decreases with increase of volume, surface energy increases with increase of surface; while, therefore, a gas occupies as large a volume as is possible under the conditions, a liquid tends to form as small a surface in contact with its vapour as is possible under the circumstances. A liquid left to itself assumes a spherical shape, and the surface tension exerts a pressure upon it, until it is in equilibrium with the volume elasticity of the liquid. Geometrical considerations show that this pressure is inversely proportional to the radius of the sphere and directly proportional to the surface tension. The latter is so small that the pressures are not large so long as the drop is large enough to be visible to the eye; but when the drops are microscopic, or even smaller, the pressures become considerable.

In accordance with this a very small drop must have a larger density and other specific properties than a large drop. The nature of a substance is changed by surface energy just as it is changed by heat, but to an insignificant extent, unless the specific surface is large (p. 474).

As the energy of the surface is greater than that of the mass of liquid, the surface condition may be regarded as intermediate between that of liquids and vapours, and it has already (p. 80) been pointed out that this is the case. Small drops have also a greater vapour pressure than plane surfaces. Similar considerations hold for solids also, and with increasing subdivision they will approximate in nature to liquids or vapours. Thus, salol, which is a solid, when ground up with an indifferent powder (quartz) is unable to induce the crystallisation of fused salol (Ostwald, 1905), although its presence is analytically recognisable. Very fine powder of a solid has a lower melting point than large pieces. For the melting point is the temperature at which the two phases have the same vapour pressure. As the fine powder has the greater vapour pressure, its vapour pressure curve will intersect the curve for the liquid at a lower temperature, as will be seen at once from Fig. 21, p. 103 (Pawloff, 1908).

Capillary Pressure.—Capillary pressure can be calculated by means of the principle of virtual changes of energy. Consider a liquid under a given pressure p contained in a vessel which is connected by means of a very narrow tube with a spherical drop of the same liquid. Owing to surface tension the surface and consequently the drop will strive to diminish, while the pressure p tends to increase them. Equilibrium is established when the work of the pressure is opposite and equal to that of the surface tension for a very small change in the radius of the drop. The former is $p\,dv$, the latter $g\,dw$. Increasing volume in the former means loss of energy, while increase of surface means gain of energy; hence the two amounts of work are of different sign and the equation is

$$-p\,dv + g\,dw = o.$$

We have now to find out dv and dw for the same change in radius. The increase in volume of a sphere of radius r for an increase in radius by the very small amount dr can be put equal to the product of the surface of the sphere and the amount dr, the surface being regarded as covered with a uniform layer of this thickness. Since the surface is $4\pi r^2$, $dv = 4\pi r^2\,dr$. Further, the surface is equal to four "great circles," and the increase in surface of a circle due to an increase of dr in the radius is represented by a circular band at the periphery, and is equal to the product of the circumference and the width of the band dr. The circumference is $2\pi r$, the increase in surface of one circle is $2\pi r\,.\,dr$, and the total increase of area of the sphere $dw = 8\pi r\,.\,dr$. On substituting these values in the above equation, dr is eliminated and $p = 2g/r$. The pressure is therefore proportional to the surface tension and inversely proportional to the radius of the sphere.

For water with a surface tension 77 at 0°, as already given, $p = 154/r$. The pressure is in absolute units, one atmosphere being approximately one million units. A drop of water whose surface tension exerts one atmosphere pressure upon it must have a radius of $1{\cdot}5 \times 10^{-4}$ cm. *i.e.* a diameter of three thousandths of a millimetre or three microns. For other liquids with smaller surface tension the diameter will be correspondingly smaller.

As the compressibility of water is ·00005 for one atmosphere, the density of drops of water of three microns diameter is ·00005 times greater than the density of water in ordinary quantities. It is at first sight a small amount, just on the limit of measurement. But with a diameter one hundred times smaller, it mounts up to nearly one-half per cent. The other specific properties of liquids suffer change to a similar extent.

CHAPTER XXI

DISPERSE SYSTEMS

Disperse Systems.—Two phases at the least must be present if surface energy is to be a dominant factor, for the boundary surfaces between them are the seat of surface energy. On geometrical grounds the one phase will be divided into small, separate volumes, while the other will occupy a continuous space. The former is the disperse phase, the latter the dispersion medium[1] (Wolfgang Ostwald, 1907). As is the case with solutions, here too the difference is the more pronounced when the dispersion medium is in large excess; there are also transition stages where the existence of a difference is doubtful.

The simplest case is that in which only two phases are present. Then we have the following classes:

(*a*) The dispersion medium is a gas. Since there cannot be two gas phases, the second phase must be either liquid or solid. The former gives rise to a cloud, the latter to dust.

(*b*) The dispersion medium is liquid. Bubbles of gas in a liquid produce foam. Liquid in a liquid gives rise to an emulsion or a milk; solid particles give rise to a suspension.

(*c*) The dispersion medium is solid. Gas bubbles produce a scoriaceous structure. Liquids give rise to the well-known mineralogical phenomenon of liquid inclusion, and solids to solid mixtures. Mixtures of solids in the form of powder do not come into this category, for they are solid particles in air, *i.e.* dust; they are systems of three or more phases with air as the dispersion medium.

A disperse system will retain its state of division unless it is acted on by special forces. If the original distribution is not uniform, mechanical means will increase the uniformity until the limit is approached at which perfectly uniform distribution is reached. The conversion of different phases into a uniform mixture, which is so frequent an experience in the arts and in our daily life, depends on

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[1] This geometrical distinction is absent if the division or dispersion is in the form of parallel plates: threads and grains which represent the other possibilities correspond to the above description.

this fact. From a purely mechanical point of view a state of uniform distribution has no advantage over a state of non-uniform distribution, so there must be some non-mechanical cause of this constant result. In particular, once the uniform mixture has been obtained, no separation can be effected by mechanical motion, provided it does not act upon the different parts with different forces. It is not a sufficient explanation to say that the state of uniform distribution is the most probable of all the possible states, for probability is not a physical cause which places one definite result before all the other possibilities. We are forced to conclude that causes of a physical nature are at work in disperse systems, which favour the formation of a uniform distribution and prevent its destruction, which can perform work and are of the nature of energy.

That this is the case, and that the work is greater when the specific surface is greater, follows from the fact that very fine suspensions and emulsions resist the forces of gravity, and may even form spontaneously as, *e.g.* finely divided clay in water. We have here a source of energy which can do work against gravity in producing uniform distribution in a disperse system. This source of energy is probably connected with the surface energy, as it only assumes noticeable dimensions when the specific surface is very large.

The Formation of Disperse Systems.—Disperse systems are produced in two ways: two (or more) phases of finite amount are treated in such a way that their common interface is very greatly extended, or the conditions of a phase are so changed that a second phase makes its appearance in the form of a large number of single particles. As such a system contains more surface energy than the original system, the expenditure of work is necessary for its formation.

The first case includes the processes of powdering, shaking up, rubbing together, etc., in all of which larger pieces are converted into smaller ones. As is well known, these systems become more disperse the longer the process is continued, *i.e.* the specific surface increases. Although very prolonged mechanical treatment is necessary before the increase of energy confers new properties to any marked extent, such cases are known, *e.g.* ultramarine powder when wet-ground loses the power of settling down on standing. Similarly, linen and cotton fibres can be "dead-milled" in the Holländer, *i.e.* so finely divided that they will no longer felt together (for paper making), but will dry up to a horny mass. In the technical appliances used to reduce substances to a state of fine division a very large part of the work is lost in the form of heat, and the efficiency of the machine is greater when most of the work is utilised in grinding down the material, and when very little is lost in mere friction. It is a great advantage to remove the small particles at once from the field of action and to submit them to a separate treatment.

The other process, the production of a new phase, takes place, intentionally and otherwise, in innumerable instances. The formation of mist in the atmosphere, and the formation of very fine precipitates in chemical reactions are examples of it. As large or small specific surfaces may be obtained under widely different conditions, we must find out by general considerations what the most suitable conditions are (v. Weimarn, 1908).

If it were not for supersaturation phenomena, a maximum of specific surface would always result when the pressure, temperature, or chemical proportions were so changed that a new phase could be formed. As these new conditions can be established very quickly over a large extent, the new phase would be formed simultaneously all through the system, provided that there was sufficient reason for its appearance at all; and, as its concentration was finite, the specific surface would be a maximum. This is what happens in the neighbourhood of a critical point, at which supersaturation is not possible.

The case is very different when supersaturation can occur. To change the conditions in such a manner as to allow a new phase to be formed, does not in general cause its appearance; nuclei are necessary to commence its formation. This is the reason for the appearance of the new phase in larger particles instead of very small ones. For if the formation is started by a nucleus, the effect of supersaturation is to enlarge this single particle, with re-establishment of equilibrium and the prevention of the appearance of other small particles.

Now surface energy is the cause of supersaturation. Equal quantities of the substance in the two phases differ in their amounts of energy (heats of fusion or vaporisation); but if the form poorer in energy has surface energy, the difference between them will be reduced. As the amount of energy increases rapidly with increased specific surface, the new phase may be imagined to be so finely divided that there is no difference in energy between them, and consequently no reason for the appearance of the new form. If a new phase could first appear only in infinitely small particles, it could not exist at all. The fact that the spontaneous appearance of new phases is a frequent occurrence indicates that the first particles formed are not infinitely small.

The assumption has been made here that the surface tension is independent of the size of the particles. But this is not necessarily the case, for the measurements on which it is based were made on surfaces of finite thickness, and the result is limited to this case. It is possible and to some extent is proved that the surface tension of very small particles becomes smaller, in which case the surface energy will not increase to infinity on increasing dispersion, but may converge to a finite limit. This limit must lie below the change of energy for the corresponding change of phase (heat of fusion or vaporisation) (p. 81). There would then be a limit to the degree of supersaturation beyond which new small particles of the new phase must of necessity appear. Now the facts appear to indicate that there is some such limit dividing the metastable region from the labile region (p. 69). The size of the particles which separate out at this limit is determined by this limiting value.

Usually the particles will not remain of this size; since they are surrounded by a supersaturated medium, the conditions are favourable to growth, and the real particles will be larger than the theoretical ones. If dust were completely excluded and absolute uniformity in other respects secured, the condensation would be ideal, and the minimum size of particles attained.

Consequently, the best conditions for extremely fine division are: very rapid and extensive supersaturation, in order to avoid metastable states; small solubility of the new phase, so that larger particles are not formed at the expense of the small ones.

The formation of disperse systems readily takes place in the neighbourhood of a critical point, owing to the simultaneous disappearance of supersaturation and surface tension.

Separation of Disperse Systems.—As the phases of a disperse system usually differ in density, they are acted upon by gravity, the denser phase falling while the lighter phase rises. This movement is opposed by the viscosity (p. 85), the effect of which on the velocity increases as the size of the particles diminishes. A stone falls rapidly through the air to the earth, but it would remain as dust suspended in the same air for hours; in a vacuum, the dust and the stone would fall at the same rate. The constant maximum velocity of a spherical particle falling through a resistant medium is given by the equation

$$v = \frac{2}{9} g r^2 \frac{D - d}{w},$$

where v is the velocity, g the gravity constant, r the radius of the sphere, D its density, d the density of the liquid and w its viscosity. The velocity is proportional to the square of the radius, and therefore rapidly diminishes when the rising or falling particles become small (Stokes, 1851).

Any mechanical force which acts differently on the two phases has a similar effect. As mass and weight are proportional to each other, centrifugal force can be employed. As it increases as the square of the velocity of rotation, it is easy to greatly exceed the effect of gravity. The centrifuge is accordingly of great use in separating a disperse system into its constituents; for example, the very small particles of fat in milk can be separated in a single brief operation, whereas under the action of gravity many hours would be necessary.

The velocity of separation is inversely proportional to the viscosity, and is reduced practically to zero in a medium of great viscosity. For instance, the settling out of artist's colours ground in oil is prevented by the addition of a small percentage of wax to the oil, the viscosity being correspondingly increased.

Solid mixtures do not segregate, owing to their very great viscosity.

Filtration.—Filtration is a very common means of separation. Like sedimentation and centrifuging, it can only be employed if the dispersive medium is a gas or liquid, and is mainly used for liquids, because there is usually no difficulty in separating a gaseous medium owing to the great difference of density.

Filtration depends on the use of a sieve, *i.e.* a plate with holes of a definite size. Up to tenths or even hundredths of a millimetre, woven fabrics can be used; considerable uniformity of size can be attained in this way corresponding to the uniformity of the threads and of the weaving. For smaller particles filter paper must be used, the pores of which can be varied considerably in size according to the method of preparation. As a rule they retain all particles of microscopic visibility.

On the extreme limit we have the semi-permeable membranes formed by precipitation (p. 171), which not only retain the finest suspensions, but even separate real solutions, *e.g.* sugar solutions, into pure water and a more concentrated residue. It is doubtful whether they are to be regarded as sieves from a molecular point of view, for it is conceivable that they act in other ways; and cases of selective permeability have been observed which do not obviously depend on the "molecular size."

Between these two come the filters prepared by allowing gelatinous masses of varying concentration to set on a suitable coarsely-porous material (Martin, 1896). By varying the concentration of the gelatinous coating (Bechhold, 1906), we can produce any desired degree of permeability, and can carry out fractional filtrations. In this way the limit between suspensions and true solutions has been obtained.

Recognition of Disperse Systems.—All these methods of separation are obviously methods of recognition, all systems which can be separated by these means being disperse. But, just as in analytical chemistry, separation is by no means necessary for recognition, and the methods of direct proof must now be described.

The principal are optical methods. As a rule, the two phases have different refractive indices and different absorption coefficients; and, in consequence, the nature of the system can be recognised at once with the naked eye. For this the size of the particles must be not less than ·1 mm. With the aid of the microscope a size of ·00015 mm. can be recognised, *i.e.* the fourth of the wave-length of the brightest light (yellow-green). Although the laws of geometric optics appear to point to unlimited magnification, diffraction, which depends on the wave-length, causes blurring of the image and limits the range of recognition.

But much smaller particles than these cause a disturbance in the propagation of light waves, and this can be utilised to recognise and even to count the number of disturbing particles. Mixtures of two transparent substances of different refractive index scatter light, *i.e.* send it out in all directions, owing to the reflexion at the interfaces of the particles. This causes a certain loss of transparency, and the turbid or milky appearance is an indication of their heterogeneous nature;[1] for reflexion always occurs at the boundary between two particles of different refractive index.

The amount of scattering diminishes with the size of the particles, and the turbidity soon escapes ordinary observation. It is still visible, however, if a very powerful beam of light is sent through the system. When the beam is viewed from one side against a dark background even slight scattering is observed. The colour is not the same as the light used or that of the objects observed, but is blue, because of the predominating reflexion of the short waves. The light is also polarised in a plane which is fixed by the direction of the original light and by the eye of the observer, and most strongly in a plane parallel to the original direction.

If this is done under the microscope the diffracting particles are seen as bright discs on a dark ground: in this way their presence (and certain optical properties) is recognisable, but not their form. The brightness of the light is of importance, *i.e.* the brightness per unit of surface, not the absolute amount of light. Sunlight affords the greatest possibility in this direction; next comes the electric arc (Siedentopf and Zsigmondy, 1903).

The dimension finally reached in this way is five millionths mm. or 5×10^{-7} cm. But it has been certainly proved that there are still smaller heterogeneous particles.

It is highly significant that there is a continuous transition from suspensions and emulsions, which are readily recognisable as such, to true solutions (for which the laws of solutions hold), this fact indicating that the nature of both systems is the same. Or, in other words, the facts here discovered indicate that true solutions are really heterogeneous, and may therefore be regarded as mixtures of different kinds of particles in the sense of the molecular hypothesis. If we add to this the result of the investigations into the electrical discharges in gases (see later, p. 533), in which are also recognisable discontinuities or a grained structure in the submicroscopic region, it appears that the final proof of the grained or atomistic-

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[1] Liquid crystals, which have different refractive indices in different directions, are also turbid when their arrangement is haphazard.

molecular nature of matter has been obtained, after a fruitless search during a whole century. Here we do not have relations which lead indirectly to atomic methods of representation, but which can also be explained in a more general, and, therefore, more scientifically justifiable manner, and thus afford no decisive support to the hypothesis. They are experimentally demonstrated spatial differences in the nature of matter, which exclude the possibility of a continuous occupancy of space. This discontinuity is below the limit directly reached by the ultramicroscope, but is not far removed from it. The "molecular dimensions" calculated from the surface tension lies roughly between 6×10^{-9} cm. and 6×10^{-8}, while the ultramicroscope goes down to 5×10^{-7}. The gap to be bridged is only a tenth power, which is no great distance.

The Brownian Movements.—The botanist R. Brown in 1827 described a phenomenon which, so far as is known at present, always makes its appearance when a pure suspension or emulsion consisting of very fine particles is observed under the microscope. The particles may be either solid or liquid; and the phenomenon is observable with mists and dust. The only necessary condition appears to be the suspension of very fine heterogeneous particles in a medium which offers no impediment to motion (*i.e.* a gas or liquid). The particles do not require to be excessively small, about ·01 mm. is the upper limit.

Such particles do not remain at rest, but are in a state of continuous, irregular motion, the paths being longer or shorter straight lines, which follow each other in zigzag fashion. The movements are not due to diffusion equalising accidental differences of concentration, for suspensions of indifferent substances have been kept for years without any appreciable diminution of the movements. External causes appear to have been completely excluded.

The smaller the particles and the lower the viscosity of the liquid, the more rapid are the movements. Spontaneous suspension, which occurs when very fine powders are covered with water or other liquids, appears to be directly due to this effect. As this process rapidly falls off with increase in size of the particles, while sedimentation under the action of gravity increases, it is possible to draw conclusions regarding the size of suspended particles by observing whether sedimentation occurs or not.

These movements are in apparent contradiction to the Second Law. The velocity depends on the viscosity, the effect of which is to use up the energy of the moving particles. The movement continues in spite of this, unless the particles coagulate together (a suspension of vermilion had not lost its movement after two years), so that energy at rest appears to become energy in motion. As early as 1863 Chr. Wiener regarded the phenomenon as a consequence of the kinetic nature of heat, which he supposed to consist of the motion of the smallest particles of liquids or of their molecules, their impacts on the microscopic grains giving rise to the Brownian movements. This kinetic theory of heat, which was propounded in the early ages, has been extensively developed by Clausius (1857), Maxwell, Boltzmann, and by many later scientists, especially in its application to gases, in spite of the very serious difficulties encountered. Still, until recently there was wanting direct experimental proof of the necessity for such a representation, which accordingly remained an arbitrary though useful hypothesis.

If the movements of a small particle suspended in a liquid are calculated on the basis of this hypothesis, the agreement with the movements actually observed is so close that we are compelled to regard this agreement as a fairly satisfactory proof of the kinetic nature of heat. A brief account of the kinetic theory of gases will be found farther on.

The calculations were made independently by Einstein (1905) and von Smoluchowski (1906), by different methods, and differ only by the value of a numerical factor. The comparison with experimental results was made by Th. Svedberg (1906). Svedberg measured the paths of ultramicroscopic particles of platinum in different solvents of different viscosity, and compared them with the values calculated from the formulæ of Einstein and Smoluchowski. The results are given below:

Solvent.	Path observed.	Calculated from E.	Calculated from S.
Acetone	$3{\cdot}1 \times 10^{-4}$	$\cdot 71 \times 10^{-4}$	$1{\cdot}09 \times 10^{-4}$
Ether	2·0	·44	·68
Amyl acetate	1·5	·38	·58
Water	1·1	·20	·31
Propyl alcohol	·7	·11	·17

The paths calculated from Einstein's formula are roughly one-fourth the observed paths, from Smoluchowski's formula one-third. As the theoretical value of the numerical factor is obviously not satisfactorily settled, the approximate proportionality between the observed and calculated values (which remains unaffected by the numerical factor) may well be considered to be a confirmation of the theory.

Still more definite confirmation has been afforded very recently by the measurements of Perrin (1908). If an emulsion consists of equal drops of known size and density, the drops will arrange themselves under the action of gravity in the same manner as the atmosphere is arranged over the earth's surface; the densities of contiguous layers will decrease in a geometrical series, the constants of which depend on the size and the density, and also on the corresponding formula of the kinetic theory of gases (see below).

Perrin has determined the size and density, and has counted the distribution of the drops at different heights in a uniform emulsion (in the case investigated the density decreases so rapidly with the height that large differences are found within a fraction of a millimetre). He not only obtained a value for R, the gas constant, in close agreement with the generally accepted value, but has developed the method to such an extent that it is probably the most accurate value for the molecular constant obtained as yet.

Stability of Disperse Systems.—Two differently sized particles of a substance, in contact with a medium containing the same substance in solution or in the form of gas, are generally not in equilibrium. The properties of the particles depend on their specific surface, and, as these are different, the smaller particle is unstable in presence of the larger. Its vapour-pressure and its solubility are greater than those of the larger particle under the same conditions. The larger particle will gain in weight at the expense of the smaller, owing to distillation or to solution followed by precipitation. The initial difference will be increased, and the smaller particle will become more unstable; this will continue until it is used up and has disappeared.

This effect must always occur if the substance is volatile or soluble. As has been repeatedly stated, there is no reason for regarding any substance as absolutely devoid of these properties, and, according to these laws, every disperse system is essentially unstable, it being merely a question of how long the transformation takes. The time will be greater the smaller the difference between the solubilities or vapour-pressures, and the smaller the velocity of reaction; the latter depends on the specific nature of the substance.

There is one special case of stability in disperse systems—when all the particles are of exactly the same size. No one particle has any advantage over the rest, and there is no cause for change. As a slight difference in temperature or pressure affecting any particle will bring about a disturbance of the equilibrium, such a system is only in labile equilibrium, which is destroyed by the slightest change in the conditions.

Another possible case of stability occurs when the surface-tension is not independent of the size of the particles, but rapidly decreases with decrease in size. There will then be a size which would be stable against change in either direction, and which would be automatically produced in a mixture of particles of different size (provided they were below a given finite size). It has already been stated (p. 480) that this is by no means improbable.[1]

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[1] A problem, which has occupied the attention of thinkers for a long time, may be answered in a similar way. If the atomic theory is to fit the facts, it must be assumed that all atoms of the same element are exactly alike in size. Now Herschel long ago suggested that this gives atoms the character of a manufactured product, for nowhere else does Nature give us systems of a given kind which are perfectly equal as regards size. The formation of these equally sized particles may be explained as the effect of

There is one instance in which this spontaneous formation of uniform drops seems to occur. If two liquids have a critical solution-point, their solutions in the neighbourhood of the critical point have a milky appearance, and behave like emulsions. In particular, they are quite constant in this respect that they are a function of the temperature and the composition, and show no disposition to change with time (Friedländer, 1901).

Apart from these, all disperse systems are more or less liable to change. The most persistent are those in which spontaneous suspension takes place against gravity, and, therefore, remain suspended, if the suspended substance is very insoluble, and otherwise not liable to change. Emulsions of practically insoluble substances and mechanically prepared suspensions of stable solids (*e.g.* quartz) may remain unchanged for many years.

In the majority of cases disperse systems are very unstable. In addition to the causes fully explained above, in which the change is due to the formation of larger particles, there is another cause, due to the appearance at first of less stable forms. If solid mercuric iodide is precipitated from solution, the unstable yellow modification always appears first, and it changes into the red modification immediately, or in a few hours or days, according to circumstances. Similarly, most other precipitates, produced by double decomposition or by physical changes of condition, exist at first in an unstable modification, which is subsequently transformed into a stable form, the velocity depending on the conditions.

Frequently the substances in a disperse system are not themselves stable, and undergo slow chemical changes under the prevailing conditions, owing to hydrolysis, condensation, etc. In such cases the disperse system is also unstable, owing to these changes.

It will therefore occasion no surprise that, as a rule, it is impossible to prepare two disperse systems exactly alike, even though the external conditions have been kept the same, as far as it is possible to do so. They have not the definiteness of properties possessed by true solutions, but vary according to their age and past history. The data concerning these properties is obviously indefinite, and it is easy to understand how different observers have often obtained widely different results with "the same" substances.

The essential direction in which disperse systems change is that of removing the dispersity, and reducing the disperse phase to one of finite limits. We conclude, therefore, that increase in grain or size of drops, coagulation to flocks or other coherent systems, settling out on the bottom or at the top are quite regular phenomena. These changes may be accelerated or retarded by various means.

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surface-tension, as described above, under circumstances which enabled the atoms to give up still smaller particles, until they were all equal. Very recent developments of our knowledge of radioactive substances make this assumption by no means improbable.

Spontaneous separation of the disperse phase can be accelerated by any means which facilitates interchange between the individual grains or drops. Raising the temperature, addition of a solvent, sometimes vigorous stirring will do this. In analytical chemistry, where dispersity gives rise to serious difficulty in separations, these means are in constant use.

The means of increasing the stability of disperse systems lie in the contrary direction; further mention is unnecessary.

That there are other influences of a more purely chemical nature is evident from the fact that moderately stable suspensions are precipitated or coagulated by very small quantities of certain substances. This cannot be taken up until the microchemical behaviour of systems containing several substances has been dealt with.

Electrical Migration.—If a current of electricity is passed through a disperse liquid system, the particles as a rule travel in the direction of the negative current, but in some systems in the opposite direction. In this respect they are like the well-known ions of salts, and the only conclusion we can come to is that they are carriers of electric charges of the appropriate sign. The velocity of migration, too, is similar to that found in the case of ions, and seems to be fairly independent of the individual nature of the particles. It is approximately proportional to the fall of potential, and amounts to 2 cm. per volt/cm. in an hour.

The question, whether all substances in the disperse condition are electrically charged, has not yet been decisively answered. On the contrary, it has been proved in many cases that the sign of the charge is conditioned by special chemical additions to the disperse medium, and can even be reversed. There is, in this case, a neutral point, at which no migration with the electric current takes place in either direction (Hardy, 1900). These neutral systems are found to be comparatively unstable, the particles readily and quickly uniting to form larger masses, which then settle out.

This migration implies a certain amount of conductivity, for, in accordance with the general laws of electricity, an equal quantity of electricity of opposite sign must travel in the other direction. This transport of electricity is usually effected by ordinary ions; hydrion in particular always seems to appear when the particles are negatively charged. As quartz powder, for instance, when suspended in water shows negative migration, the ions of water, which are always present in fixed concentration (p. 404), appear to participate in it, one of them, hydroxidion, combining with the particles, and conferring on them the appropriate electric charge.

This is probably connected with the tendency of substances of high molecular complexity to pass readily into a strongly disperse or "colloid" state, as is also the spontaneous dispersion, or "peptisation," of these substances in the coagulated or non-disperse condition when a substance is added to them, from which they can abstract the necessary ions. As this involves the equilibrium between several constituents, it cannot be adequately discussed until the simpler phenomena which are met with in this connexion have been dealt with (see below).

Colloids.—Graham (1861) was the first to distinguish the two classes of crystalloids and colloids. In the first were included the substances hitherto treated as chemical individuals, because of their constant specific properties and behaviour when subjected to analytical methods of separation. The name expresses the fact that most of them are easily prepared in the form of crystals, though the designation is extended to substances (such as the lower members of the saturated hydrocarbons) which are unknown in the crystalline condition, but possess the other properties of pure substances.

Colloids, on the contrary, are substances, the properties of which are more or less indefinite. They differ from solutions in that they cannot be resolved into components which have the properties of pure substances. They form systems with water, alcohol, and other pure substances, which resemble solutions in some respects, but do not appear to obey the solution laws (p. 173), as solutions of crystalloids usually do, their behaviour being rather that of mechanical mixtures. This is shown in several ways; thus, the boiling-point and freezing-point of the solvent are not appreciably altered by the presence of a colloid, and the osmotic pressure of colloid solutions is very small. This has been explained by ascribing to colloids a very high molar weight, which may even be variable.

But while Graham regarded colloids as an essentially separate class of substances, recent investigations have shown it to be rather a special state into which practically all chemical substances can be brought. This state is one of very fine division or of very great specific surface. Accordingly, the above considerations, which were expressly developed in reference to systems of great dispersity, apply directly to what Graham called colloids. The distinction really is in the ease with which substances can be made to assume this state. One reason why substances do not always appear in the colloid state when they are formed as a second phase within a liquid (or gas) has been given already (p. 480); another reason is that the coagulation of disperse phases is extraordinarily accelerated by the presence of any salts in the solution. As most precipitations are reactions between salts, usually the conditions for the precipitate assuming the disperse state do not obtain. If the conditions are suitable, the substance is obtained in the colloid state.

The best-known example of this is arsenious sulphide, produced by the addition of hydrogen sulphide to an aqueous solution of arsenious acid. As no salt is present, a "colloid solution" is obtained, *i.e.* a liquid mixture, in which the second phase, arsenious sulphide, is in extremely fine division. The electrical disintegration of metals is another instance (Bredig, 1898). The metal is vaporised by the electric current, owing to local heating, and the instantaneous condensation of the vapour by the surrounding liquid causes the metal to appear in the colloid state, which is more or less stable as there are no salts present to cause precipitation.

Certain substances which have been coagulated by salts pass into the colloid state when these salts are removed by washing. This is the cause of many precipitates "passing through" the filter in analytical operations, when the greater part of the salts have been washed out. This is prevented by washing the precipitate with a suitable salt solution instead of with pure water, *i.e.* the coagulated state is preserved.

While some substances readily regenerate the colloid state in contact with pure water, others retain their insolubility even after washing out. This really depends on the velocity with which the precipitate passes from the highly disperse state into larger grains or crystals. If the velocity is small, the possibility of passing into the colloid state is retained for a longer time. By assigning somewhat arbitrary limits of time, *e.g.* a few days or weeks, the distinction has been made between reversible and irreversible colloids, the former comprising those which can be reconverted into the colloid state after coagulation. As, however, the colloid state is itself an unstable state, all colloids are to be regarded as irreversible, and the difference is really a practical one, useful in describing their time phenomena, but without theoretical foundation.[1]

There is a difference between various colloid liquids which must not be overlooked. In those in which it is fairly certain that the disperse phase is solid (metals, metallic sulphides, clay, etc.), the properties of the dispersive medium are scarcely affected; the viscosity in particular is practically unaltered, while in others, such as gelatine, gum, agar-agar, dextrin, and silicic acid, the reverse is true. They produce a great alteration in the viscosity, and often "set" to trembling jellies, which possess form energy, or elasticity, and are so far like solids. It is very probable that in these cases the second phase is also liquid (or at least half-liquid), and it has been shown that solidified gelatine consists of a spongy framework of concentrated gelatine, in which a dilute solution is encased. There are thus two liquid phases of limited mutual solubility (p. 323), which are very probably in the neighbourhood of their critical point, where they become completely soluble in each other.

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[1] Colloids are also called reversible, if they are easily transformed from the one-phase system or the solution into the colloid two-phase system, by, for instance, change of temperature. But this is undoubtedly a totally different phenomenon, for the second disperse phase is made anew each time. Gelatine is a well-known instance of this; it forms a solution with water at higher temperatures, and a colloid when it sets at lower temperatures.

The great viscosity of the liquid phase is probably connected with the fact that the viscosity of a liquid rapidly increases with the number of hydroxyl groups, especially in organic compounds. A comparison of alcohol, glycol and glycerol, or of propionic acid and lactic acid, shows this. There is the further circumstance that the viscosity of solutions is very high in the vicinity of the critical solution point of two liquids. The great viscosity of solutions of gum and of dextrin must not be confused with the semi-solid or jelly-like character of gelatine or agar-agar. The former is not altered by stirring or other mechanical disturbance; the latter is destroyed by these means.

The Size of Disperse Particles.—As already stated (p. 475), surface energy might be expected to produce appreciable differences in the properties of disperse systems when the size of the particles falls below 10^{-4} cm. This is about seven times larger than the limit of microscopic visibility. Some of the associated phenomena, *e.g.* the molecular motion, commence at about 10^{-3} cm., which is probably the extreme upper limit at which the properties peculiar to disperse systems begin to show.

From this point to the limit of microscopic visibility, which may be put at 10^{-5} (this is a little excessive), we have the first stage of microscopic particles. In Zsigmondy's nomenclature they are known as microns.

This is succeeded by the region of ultra-microscopic visibility, the limit of which is determined by an extraneous circumstance, the intensity of the available light. As at the present time no light of greater "brightness" than the sun is available, the limit is about 5×10^{-7} cm. These particles are submicrons.

The isolated existence of still smaller particles, which was to be expected considering the accidental nature of the limit, has been demonstrated in other ways. Zsigmondy (1906) has shown that preparations of reduced gold, in which the particles are invisible under the ultra-microscope, accelerated to an extraordinary degree the formation of submicrons in suitable solutions; this effect he attributes to individual but still invisible particles of gold, which act as nuclei in the supersaturated solution, and increase in size at the expense of the gold there present. These particles are called amicrons. He estimated their size in a given preparation at a little over 10^{-7} cm., but this is probably not the lower limit.

The kinetic theory places the size of gas molecules at about 10^{-8} cm. There is thus unbroken continuity. The limit of spatial discontinuity which is physically observable is still lower, for electrical phenomena take us at least a further power of ten.

CHAPTER XXII

SPECIAL MICROCHEMISTRY

Differences of Concentration at the Surface.—So far our considerations have been based on the general facts of surface energy, without inquiring into its special modes of action. Nevertheless it was frequently necessary to refer to these. We must now turn to the material effects produced by surface extension.

As surfaces and interfaces are the seat of a special form of energy, the properties of substances in these surfaces must be different from those exhibited by larger quantities, for properties are only affirmations of the kinds of energy present. The properties of surfaces can seldom be directly investigated, as they are limited to the very thin layer of about 10^{-8} cm., which cannot be treated separately apart from the main mass. There are, however, a number of cases where a certain amount of investigation is possible. The most important are the alterations of concentration or density of substances in surfaces.

These changes are most accessible where differences of concentration are most easily produced. For uniform substances this presupposes the gas state, and we are thus led to consider the effect of diaphragms on gases. There is in general a condensation of the gas at the surface. Although it must also occur on liquids, it can only be recognised on solids, because the technical difficulties in the way of maintaining the foam of liquids for the necessary length of time have not yet been overcome. The condensation of gases on the surfaces of solids is a well-known fact. As it is proportional to the surface, the amount escapes observation unless the specific surface is large, as in powders or solids of cellular structure.

Similar phenomena are observed when solids with large specific surface are brought into liquid solutions. Frequently the solute accumulates in the surface; the surface tension plays an important role here.

These two phenomena, which are very similar even to the extent of the laws governing them, are known as adsorption, in order to distinguish them from absorption or the solution of gases in liquids, to which they have a certain amount of likeness. The essential difference between them is that in the one the action is proportional to the surface, in the other to the quantity or volume of the recipient substance.

Finally, a liquid solution will have a different composition in its "free" surface, *i.e.* at the interface between it and its own vapour, than in the interior of the solution, the component (or a product) with the smaller surface tension being more concentrated in the surface. For every free surface tends to diminish its energy. This can be accomplished by diminishing either the capacity factor, the surface (as usually happens), or the intensity factor, the tension. The latter can happen in solutions, but not in pure liquids. In a solution the substance with smaller surface tension will pass into the surface, until the work necessary for its transference is as great as the corresponding diminution of the surface energy.

Gas Adsorption.—A solid, when placed in a gas, at once condenses or retains a certain amount of the gas so that this part exerts no pressure; the amount is proportional to the surface, and depends further on the temperature and pressure, and on the nature of the substances. The amount adsorbed per unit surface (1 sq. cm.) is extremely small, and is inappreciable except on large surfaces. There are not many absolute measurements of it. It is not very different for different gases; about three times as much ammonia is adsorbed as hydrogen (by volume); these gases form the extreme limit of observation. The absolute amount is about 10^{-7}g per sq. cm. This is of the same order as the concentration of the surface layer in pure liquids (p. 83).

Consequently these phenomena are not easily observed at the ordinary surfaces of solids, as the amount of gas taken up is too small; they are only measurable when the solid is porous or finely powdered, and thus presents a large specific surface. In a few cases a sufficiently large surface of known extent was obtained by using bundles of glass threads, the surface of which was calculated from the length and weight (the density being known) on the assumption that the threads were cylindrical. Usually investigators have been content to use porous solid substances such as charcoal, meerschaum, etc., it being assumed that they are so uniform in texture that the active surface is proportional to the weight, *i.e.* that the specific surface is constant. This assumption has usually been found to be justified when parallel experiments have been made. If necessary, uniformity can be assured by mechanical means (sifting or elutriation of the material).

The typical form of experiment is as follows: the solid is brought into a glass vessel which is connected with a gas-measuring apparatus, and is then freed as completely as possible from surface layers.

This is best done by pumping out at a high temperature. Although the greater part of the surface layer is easily removed by this means, a small residue is tenaciously retained. This is quite noticeable if there are means of recognising very small quantities, as in Geissler tubes, through which electric discharges are passed. It is extremely difficult to remove surface layers from glass (*e.g.* water vapour) so completely that they cannot be recognised in the spectrum. Measured quantities of the gas are then admitted, and after some time the residual volume is measured. The observation is repeated in order to ascertain if adsorption is practically complete, or still continues. As the process, like all similar ones, follows a logarithmic function, *i.e.* the velocity is proportional to the momentary distance from saturation, observation of the first stages of the process affords some idea of the velocity, and of the time necessary for practical completion of the reaction.

In this way an equilibrium is obtained, which is the same whether the pressure has been reduced or increased. This circumstance, that the same equilibrium has been reached from both sides, is a guarantee against a very slow irreversible process being mistaken for a real equilibrium.

This phenomenon is, as already stated, known as adsorption. So far as is known, it is accompanied by evolution of heat; in consequence of this, it is smaller at higher temperatures. Use is made of this fact, as described above, to remove adsorbed gases from solid surfaces.

The quantity of gas adsorbed by unit surface is a function of the pressure. Attempts to apply Henry's law are unsuccessful; the amount of any gas adsorbed increases much more slowly than the pressure. This explains the difficulty in removing the last (or first) traces of adsorbed gas from a surface. If the pressure is halved, a smaller fraction than one-half of the gas is removed; if it is again halved, the same fraction is again removed, and thus the pressure is reduced much more rapidly than the residue of gas.

This connexion between pressure and quantity of gas adsorbed, each being arranged in a geometrical series with a different exponent, is the quantitative relation between pressure and surface density. Denoting the pressure by p, the surface concentration by b, the formula is

$$p = kb^m,$$

where k and m are constants depending on the temperature and the nature of the substances. If Henry's law was valid, m would be $= 1$.

In reality m is always greater than 1, and under certain circumstances (for solutions) may be as high as 10 or 12. This excludes the possibility of regarding the process as a distribution equilibrium

(p. 375), for, if it were, there must be a change in molar weight at the surface of the solid, of such a nature that one mol of the gas gives rise to m mols of the adsorbed substance. In most cases reactions of this kind are excluded on chemical grounds.

The cause of adsorption is rather to be found, as previously stated, in surface-energy. There is a surface tension in the surfaces of solids, as in liquids, *i.e.* the surface tends to diminish, and its formation requires the expenditure of work. This is the cause of the tensile strength and rigidity of solids. This surface tension changes, becoming smaller, when the surface is covered with a layer of adsorbed gas; the process therefore continues spontaneously until the virtual work for the compression of the adsorbed gas on the one hand balances that for the diminution of surface energy on the other. As no method has yet been discovered by which the surface tension of solids can be accurately determined, it is impossible to go more deeply into this matter from the experimental side.

Adsorption from Solution. — Similar phemomena are observed when a solid substance is brought into contact with a solution. At its surface, too, is established a definite surface-concentration which is in equilibrium with the concentration in the solution. In this case there are very considerable differences in the amount adsorbed, the quantity appearing to depend on the nature of the adsorbed solute rather than on that of the solid, since substances of small surface-tension preponderate in the surface, and thus are adsorbed (Freundlich, 1906). The same relation

$$c = kb^m,$$

in which c is the concentration in the solution, b that in the surface, holds between the two concentrations. The value of the exponent m varies very much, but is always greater than 1.

These phenomena have been long known, and are often of technical importance. For instance, the dyeing of fabrics is, at least in part, an adsorption process, although in certain cases there are undoubtedly coupled with it more strictly chemical processes. We are not justified then in speaking of a "theory of dyeing" as if any single theory can be applied to all the processes of dyeing. Dyeing is not a scientific, but a technical notion, which denotes uniform results without regard to the means employed. Science is bound to take into consideration the means, and, if they are found to be different, it must put forward correspondingly different theories of the dyeing processes which depend on them.

Another technical application of adsorption is the decolourising of impure solutions by means of charcoal, kieselgur, and other materials of great specific surface. In many cases coloured impurities are especially adsorbable by these substances; and to remove these foreign substances from solutions, the solutions are shaken up with finely-divided charcoal, etc. Of course, uncoloured substances are also taken up if they, too, are easily adsorbed.

In analytical chemistry, also, it is of importance; for it renders the washing of precipitates more difficult. Application of the considerations on p. 494 to the case of solutions shows at once that the removal of the last traces of adsorbed solute will require a very large amount of solvent.

The relation $c = kb^m$ has been experimentally proved by bringing solutions of known concentration into contact with known weights of charcoal, fibre, clay, etc., and allowing equilibrium to be established between them. Equilibrium is rapidly attained, especially at high temperatures, but, as in so many cases, the velocity depends very much on the nature of the substances concerned. If a more concentrated solution is employed at first, and is diluted after approximate equilibrium has been attained, the equilibrium point is approached from the other side and, in general, in much less time. The effect of temperature is usually small, corresponding to a small heat of adsorption under these conditions. The heat of adsorption has not yet been measured directly.

The cause of the adsorption is again to be found in surface energy, but here the matter is more complicated since it is the resultant of several energies of this kind. First of all, for a liquid to wet a solid, the following relation must be present. The free surface of the solid will be diminished by the wetting, and at the same time the interface between the solid and the liquid, as well as that between the liquid and air or its own vapour, will be increased. Work is gained from this series of processes, for otherwise they would not take place spontaneously, and as the resulting and disappearing surfaces are equal, there must be a corresponding relation between the surface tensions. Denoting the surface tension of solid in gas, or its "free" surface tension, by (sg), that of the solid in liquid by (sf), and that of the liquid in gas by (fg), we have $(sg) > (sf) + (fg)$. Wetting can only occur when the free surface tension of the solid is large, and that of the liquid is smaller. Adsorption occurs when the surface tension (sf) is diminished by the transference of the solute from the solution to the surface. We have here the same cause as in adsorption of gases; equilibrium is attained here also when the work against the osmotic pressure is equal to that gained by the diminution of the surface tension, both being referred to equal quantities of substance.

These simple relations are frequently masked by more complex processes of a chemical nature, by which the adsorbed substances undergo changes, lose their solubility, and cannot be washed out again. These changes are especially valuable from the dyer's point of view, who seeks to secure or promote them. They have given rise to the never-ending dispute "whether dyeing is a chemical or a physical process." As the alternatives are not mutually exclusive, the question in this form is doomed to failure. But it is so, because in this region the difference is indefinite and fluctuating, and depends upon arbitrary definitions. A more definite question is whether dyeing is a pure adsorption or whether other processes play a part in it. The answer is undoubtedly that there are dyeings which are based upon adsorption alone, and many more in which other factors are concerned. It is the object of science to discover these factors and the laws which regulate them.

The Surface of Solutions.—In addition to the energy taken up by the formation of an interface between it and the vapour, liquid solutions undergo another surface change, which consists in a difference of composition between the surface and the interior of the solution. If we imagine a surface of the same composition to be formed, it will not in general be in equilibrium with the interior. If, for instance, one component of the solution has a very small surface tension, the energy of the surface will be smaller if an excess of this substances enters the surface, and consequently reduces the surface tension. Such a substance will pass into the surface until the work necessary to withdraw it from the solution is exactly balanced by the work gained by the corresponding diminution of the surface tension. The tendency will thus be for substances of small surface tension to pass into the surface, and even when they are present in small quantity to become relatively more concentrated in it, with a corresponding reduction of the tension. Conversely, a substance with great surface tension will have no effect on the surface tension of the solution, when it is present in the solution along with others of small surface tension, for it cannot enter the surface, because this would increase the surface tension; this would require an expenditure of energy, which is not available, because removal of it from the solution also requires work instead of giving it up (W. Gibbs, 1874).

This is fully borne out by the experimental results. Water is a substance with a great surface tension, and it has long been known that very small quantities of impurities of small surface-tension have a very large effect on water. There were difficulties in the way of determining this magnitude for water and solutions in water; they have been overcome by frequent renewal of the surface, and by adequate protection of the surface against impurities.

Direct proof of this accumulation of such "active" substances in the surface layer is not easy, as the quantities are so very small. Even when the surface layer is very different in concentration from the interior, the thickness of the surface layer is very small, and cannot be treated by itself, but only in conjunction with a fairly large quantity of the interior liquid. When the latter was reduced as far as possible by making bubbles, the separation was sufficient for analytical purposes, and the difference of concentration was demonstrated directly (Zawidski, 1900).

The Surface Concentration.—If we have a given amount of the solution, the volume of which is v, the surface w, the volume concentration of the solute c, and the surface concentration k, the total amount of solute is $M = cv + kw$.

This assumes that the substance in the surface occupies no space at all. There is really a layer of finite, but very small thickness next the surface, in which the total concentration is different from that in the interior. To take this into account, the surface concentration is defined as the excess (it may be negative, *i.e.* a deficit) of solute present in a sheet of finite thickness, which contains the surface, over the amount of solute it contains in virtue of the volume concentration. This excess is clearly independent of the thickness of the sheet taken, for the inclusion of further layers only introduces a volume in which the concentration is exactly equal to the volume-concentration, and therefore vanishes on subtraction.

This is evident if the question is asked how the surface concentration can be measured. As volume and surface are always present simultaneously, it appears at first sight impossible to determine the two concentrations separately. But the surface can be increased to any desired extent, the volume being kept constant, by stretching some of the liquid into a thin sheet or bubble, or by dividing it into a very large number of smaller drops. If such differently formed systems are prepared in such a manner that their volume concentration is always the same (*e.g.* by separating them from a very large volume of solution), the total concentration will increase proportionally to the surface. If G_1 is the total concentration for the surface W_1, and G_2 that for the surface W_2, $\frac{G_2 - G_1}{W_2 - W_1}$ is equal to the surface concentration.

Performance of these determinations is greatly facilitated by the circumstance that surface concentrations have usually very small absolute values. For masses of liquid of such a shape, that no one dimension much exceeds the rest, the total concentration can at once be put down as the same as the volume concentration. Only when the form is that of thin leaves, threads or dust, where one dimension (or two or three) is very small, does the specific surface become sufficiently large to make its difference of concentration of any account. In the above equation W_1 is so small in comparison with W_2 that it can practically be put down as zero.

This definition of surface concentration does not presuppose any knowledge of the distribution of the solute in the interface. The concentration difference obviously cannot be reduced to a mathematical plane, and it seems probable that the properties of the surface pass continuously into the properties of the interior, so that there is no really sharp line of demarcation between the surface layer and the rest. On the other hand, it is experimentally known that the surface differences make themselves felt only at very slight depths; this follows from the fact that the surface tension of soap films, down to very thin layers, is independent of their thickness. So long as this is the case, the thickness has plainly not reached the variable region, and the latter must be thinner than half the thickness of the film, which of course carries a surface on each side. The dimensions within which this transition from the surface layer to the uniform interior is complete are probably a little above the calculated thickness of the capillary surface layer of pure liquids (p. 83), viz. about 10^{-8} cm.

The Concentration Formula.—Suppose a solution bounded by a surface so large that the surface contains unit weight of the solute in consequence of surface concentration. This surface is W, and its tension is g. Let the transport of a very small quantity of solute into the surface decrease the tension by dg, the energy change for this process amounts to W dg.

This energy must just suffice to cover the work necessary to remove the same quantity of solute from the interior; the latter amounts to v dp, where v is the volume of unit weight, and dp is the change in pressure caused by its removal. If the laws of dilute solution are assumed to hold, the volume for one mol is RT/p, and for unit weight it is RT/mp, where m is the molar weight and p is the osmotic pressure. The sum of the two energy changes must be zero, and we have

$$\mathrm{W\,dg + RT\,dp/mp = o, \text{ or } dg/dp = -RT/Wmp.}$$

As dp is proportional to the concentration, this formula gives a connexion between volume concentration and surface tension. It is very similar in form to the relations between vapour pressure and temperature (p. 79) or electromotive force and temperature (p. 434). To test it, the variation of surface tension with the volume concentration of the solution must be known, and also W, the surface, in which the unit weight of solute is found in virtue of the surface concentration. This is the reciprocal of the surface concentration k, as it is the surface of unit quantity, while the surface concentration is the quantity in unit surface: $W = 1/k$.

The determination of the latter values is very difficult, and is not very accurate. Experiments in this direction (Milner, 1907; Lewis, 1908) have only yielded agreement in the sign of the change, while the numerical results differ very considerably. No cause of this want of agreement is yet known.

The qualitative meaning of the formula is as follows. Since R, T, m and p are all positive, the sign of the ratio dg/dp depends on the sign of W, or of the surface concentration k, as both are of the same sign. When dg/dp is positive, k is negative, and conversely. If the surface tension increases with increasing concentration of the solute, the surface concentration of this solute is negative, *i.e.* there is less of it in the surface than there should be in virtue of the volume concentration. If, on the contrary, the surface tension decreases with increasing concentration of the solute, the surface concentration is positive, *i.e.* there is more of solute in the surface than corresponds to the volume concentration.

The first case occurs in aqueous solutions of the strongly ionised inorganic salts, the second case in most solutions of organic compounds, which themselves have always a smaller surface tension than water. We may conclude from this that ions do not readily enter the surface, if at all, while indifferent substances in the main seek the surface. The latter affect the surface tension of the solvent much more than the former.

It may be added, in conclusion, that in the adsorption of gases as well as of solutes by solids, the surface tension of the solid is diminished, since a positive surface concentration results. A negative one would be very difficult to observe.

Adsorption by Colloids.—The great surface extension of disperse systems provides an exceptional opportunity for the display of adsorption phenomena, with the result that many phenomena are to be traced to this cause. They include the powerful effect frequently produced by very small quantities of substances on the properties of colloid solutions.

The most frequent is the precipitation or coagulation of the disperse phase by the addition of electrolytes. During this process the molecular motion ceases first of all, the particles unite to larger ones, which fall to the bottom. Stoppage of the molecular motion appears to be the primary cause of this complex phenomenon, for it has frequently been observed that the motion ceases immediately after the addition, before the particles have had time to unite to larger masses. The added eloctrolytes are found in the precipitate: this makes the assumption probable that the action is chemical, for, as ions increase the surface tension and therefore do not go into the free surface, they are not likely to accumulate at the surface of the suspended particles by simple adsorption.

On the other hand, all solids in the disperse condition appear to undergo this reaction, whatever their chemical nature may be; colloid metals and metallic sulphides show it as well as clay, quartz, ultramarine, and gum mastic.[1] As all these substances have some

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[1] According to some preliminary experiments an emulsion of vaseline (saturated hydrocarbons), made by dissolving it in alcohol and pouring the solution into a large

of the characters of ions in virtue of their electrical migration, there is always the possibility of chemical action.

The activity of salts depends on the anions or kations, according to whether the suspension is positive or negative, as indicated by the direction of its electrical migration; univalent ions must have the greatest concentration to produce precipitation, bivalent ions a less concentration, and trivalent ions still less. The differences are very great, and can be expressed approximately by a formula of the form $a\ e^n = \text{const.}$, where n is the valency. Still there are pronounced specific effects. The ion of opposite sign is alone concerned in the precipitation, the other ion being of no account.

Colloids of opposite charge also produce a similar precipitation of each other. But here (as is the case with salt precipitation too) there are many complications depending on the concentration. They are not gone into here, as they have not yet been satisfactorily explained.

Non-electrolytes do not usually cause coagulation, except at greater concentrations.

Colloids like gelatine (in which therefore the disperse phase is liquid) exert a marked protection of suspensions against the coagulating agents mentioned above, as even at very small concentrations they prevent the union and precipitation of the particles. The same effect is observable in the formation of such disperse forms; sparingly soluble salts, which in the ordinary precipitation by double decomposition are immediately coagulated by the other ions present (as, *e.g.* the silver halides), remain in suspension when the precipitation takes place in the presence of gelatinous substances. Thus, for instance, silver chloride forms a transparent emulsion if only one per cent of gelatine is present in the precipitating solutions (silver nitrate and sodium chloride). Extensive use is made of this in the manufacture of silver bromide gelatine plates for photographic purposes.[1]

This protective action is probably connected with the small surface tension of the substances in question, which enables them to clothe the particles of the solid phase, and so isolate them from each other (Bechhold, 1904). Something similar to this certainly takes place with emulsions; while an emulsion made by shaking

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quantity of water, which showed molecular motion very well, was very insensitive to additions of salts. It neither lost its motion nor coagulated.

[1] Silver bromide as first precipitated in the presence of gelatine in a state of very fine-division is too insensitive for photographic purposes. It has to be "ripened" by prolonged digestion in the heat or in presence of ammonia, thus increasing the size of the grains by recrystallisation. The ripening may probably be a chemical process quite independent of this, and may depend on incipient decomposition of the silver bromide by the gelatine. The same effect may probably be produced by applying other substances without producing the undesirable increase in the grain.

up pure oil and water very soon separates out again into its components, it remains stable when a little saponin, soap, gall salts, or other substances which go into the surface layer, is added to the water. The making of butter, too, depends on the destruction of the caseïn layers, which protect the globules of butter; when these are destroyed (by the acid produced), the globules can unite.

CHAPTER XXIII

THE KINETIC THEORY OF GASES

Pressure and Volume.—The exceedingly simple mechanical properties which make themselves evident in the uniform comportment of gases towards changes of temperature and pressure have from the first invited attempts to deduce them as necessities by means of some simple mechanical construction. As far back as 1738, Daniel Bernoulli worked out a conception in agreement with that in vogue at the present day. Yet only recently, and in especial by the work of Clausius and Maxwell, has its scope been widened, and applications of it made to various phenomena.

The fundamental phenomenon is the expansive tendency of gases, in virtue of which they fill uniformly any space offered them. No intelligible results were arrived at so long as the existence of a repulsive force between the gas molecules was assumed from analogy with the attractive force of gravitation acting through space. Only when the property in question was conceived as a pure phenomenon of motion was the framing of an intelligible hypothesis followed by success.

According to this hypothesis a gas consists of a large number of small particles which do not remain at rest each in its place, but move about amongst each other with great velocity. In consequence, as soon as free space is offered to a gas, the molecules already in motion towards that space fly into it, with the result that it is very rapidly filled with the gas. In virtue of this continual movement there is on the average the same number of molecules per unit volume in every part of the space occupied by the gas, *i.e.* the density is everywhere the same.

As the movements take place in all directions, it must happen that molecules in rapid motion reach the walls of the vessel in which the gas is enclosed, rebound from them, and fly back into the interior. Through these continual impacts the gas exercises a pressure on the walls, which manifestly must increase both with the number of molecules and with the mass and velocity of each.

To find this pressure, let us imagine a cube whose side is equal to l. Let the number of molecules the cube contains be n, and let them be all of the same kind, each having the mass m and moving with the velocity c. Finally, let the motions take place similarly in all directions.

We consider first one molecule which is flying in any one direction with the velocity c. According to the laws of kinematics, we may decompose this velocity into three components x, y, and z at right angles to each other, which are connected with c in the same way as a rectangular parallelopiped to its diagonal, viz. $x^2 + y^2 + z^2 = c^2$.

Let the three components be parallel to the edges of the cube. The action which the molecule exercises in striking a side of the cube in the slanting direction with the velocity c is equivalent to that which it would exercise if it reached the same place with the component velocity perpendicular to the wall in question. If we consider in the first place the component x, then this action is equal to $2mx$, because on striking it must first lose the momentum mx and then assume the same quantity in the opposite direction when it rebounds, the elasticity being perfect.

This action of a single impact will take place $\frac{x}{l}$ times in unit time against the two parallel faces of the cube, *i.e.* as many times as the distance x in unit time is divisible by the distance l between the faces of the cube. The total action of a molecule in the unit of time will therefore be equal to $\frac{2mx^2}{l}$.

The same holds for the two other components, so that the action of one molecule in unit time on all the faces of the cube will be $\frac{2m}{l}(x^2 + y^2 + z^2)$, or, according to the above equation, $\frac{2mc^2}{l}$; and of all the molecules, $\frac{2mnc^2}{l}$. To find from this the pressure p per unit of surface we must divide it by the total surface exposed to the pressure, which in this case is $6l^2$; it follows that $p = \frac{2mnc^2}{6l^3}$, or, as l^3 is the volume of the cube v

$$pv = \frac{1}{3}mnc^2.$$

This is the relation developed on the basis of the hypothesis given above as to the mechanical constitution of gases. As in the right-hand member of the equation we have for a given quantity of gas only constant values, it follows that the product of pressure and volume in such a mechanical system must also be constant, and so we have Boyle's law.

The extension of this proof for the cube to a vessel of any form can be made without difficulty, since the latter may be supposed built up of small cubes. The internal walls experience equal pressure on both sides, and thus may be imagined altogether absent without the system being changed.

Temperature.—The quantity mn in the last equation, since it is the product of the mass of one molecule into the number of molecules, is equal to the whole mass of the gas. Half the product of a moving mass and the square of its velocity, $m\frac{c^2}{2}$, is called its kinetic energy. Now we can write our equation in the form

$$pv = \frac{2}{3}mn\frac{c^2}{2},$$

so that the result may be expressed thus: The product of pressure and volume of a gas, or its volume energy, is equal to two-thirds of the kinetic energy of its molecules.

If, therefore, we have different gases at the same volume and pressure, the total kinetic energy of their molecules must be the same.

This evidently holds for every value of the kinetic energy. If now we alter the temperature of a gas, either its pressure or its volume will alter, in general the product of the two. As of the two factors of the kinetic energy, viz. mass and velocity, the first can undergo no change, it is clear that with a change of temperature there must be a change of velocity, and the square of the velocity is proportional to the absolute temperature.

Two gases are in equilibrium as regards temperature when they do not influence each other on contact with respect to pressure and volume. If we now ask under what circumstances two mechanical systems such as we suppose gases to be, exert no influence on each other (the masses of the moving particles being different), dynamics teaches us that this happens when the kinetic energy of the moving particles is the same; the actual calculation is too involved to be given here. Equal changes of temperature, therefore, in different gases correspond to equal changes of kinetic energy. As, however, on the other hand, the product pv is always proportional to the kinetic energy, it follows that in different gases equal changes of temperature cause proportionate changes of the product pv. This is no other than the law of the expansion of gases in its most general form, and so it also may be represented as a consequence of our mechanical assumptions.

The Number of Molecules.—Lastly, we may deduce Avogadro's law that in equal volumes of different gases there is under the same conditions the same number of molecules. If p_1 and v_1 be the pressure and volume of one gas, and p_2 and v_2 be those of a second, and further, if $p_1 = p_2$ and $v_1 = v_2$, then $p_1v_1 = p_2v_2$. Now it has been shown that $pv = \frac{2}{3}mn\frac{c^2}{2}$, so we have, omitting the factor $\frac{2}{3}$ on both sides,

$$m_1n_1\frac{c_1^2}{2} = m_2n_2\frac{c_2^2}{2}.$$

According to the proposition mentioned above two gases have the same temperature when the kinetic energy of their individual molecules is the same, *i.e.* when

$$m_1\frac{c_1^2}{2} = m_2\frac{c_2^2}{2}.$$

Dividing the first equation by this one we get

$$n_1 = n_2,$$

i.e. if the pressure, volume, and temperature of two gases be equal, then the number of molecules in each is the same. We thus arrive in a perfectly independent, although hypothetical, way at the same conclusion as we reached earlier as being the most probable expression for the chemical facts.

Velocity of Molecules.—The relations just developed may, lastly, be used to calculate the velocities with which the molecules of different gases must move in order to exercise the pressure actually observed. The equation $pv = \frac{1}{3}mnc^2$ gives when solved for c the expression $c = \sqrt{\frac{3pv}{mn}}$.

If we consider 1 g. oxygen at 0° and 76 cm. pressure, the mass mn is in the first place $= 1$, and the volume of 1 g. oxygen under these conditions is $v = 699{\cdot}8$ (p. 42). The pressure is equal to 1013130 absolute units. If we perform the calculation we find

$$c = 46100.$$

A molecule of oxygen moves, therefore, through space under the given conditions with a velocity of 46100 cm., or over a quarter of a mile per second.

In the formula $c = \sqrt{\frac{3pv}{mn}}$, the quotient $\frac{mn}{v}$ or the mass divided by the volume, is simply the absolute density. If this be represented by s, we have $c = \sqrt{\frac{3p}{s}}$; the molecular velocities of gases are inversely proportional to the square root of their densities.

We have no means of observing these velocities directly, but if different gases be allowed to stream through a small opening in a thin wall, the velocities with which they do so are inversely proportional to the square root of their densities. This is indeed no direct support to our hypothesis, for a general dynamical consideration shows that this must be the case, without any assumption as to the constitution of gases being made at all. It is, however, noteworthy that the kinetic theory of gases, in so far as the velocity of effusion is considered as conditioned by the velocity of the molecules, leads to the same conclusion.

It might be asked how, in spite of these enormous velocities, a strongly smelling gas developed in one end of a moderately large room filled with still air is not immediately perceptible at the remote end, but requires a sensible time to arrive there. In fact, this question has been raised as a decisive objection to the admissibility of the kinetic theory.

Clausius answered it by drawing attention to the circumstance that though the molecules actually possess such velocities in their free paths, yet these free paths are in all probability very short on account of the frequent collisions of the molecules with each other. The actual path of a molecule is thus not a long straight line, but an irregular zigzag composed of very short straight lines, on which the molecule, despite its great velocity, is in general not far removed from its starting-point.

A second question is, whether, if this be the case, it is admissible to assume that all the molecules of a gas have the same velocity. By such incessant collisions some molecules must evidently acquire a greater velocity and others a smaller, so that in general at a given instant there will be all possible velocities in one and the same gas.

We must grant this. But the above deductions still hold, if we determine the velocity c, so that the total kinetic energy of the molecules, if they all had this same velocity c, would be equal to the kinetic energy they actually possess. Instead of the expression "kinetic energy" we should, strictly speaking, substitute "average kinetic energy" in the above deductions. This of course does not in any way alter the general results arrived at.

Clerk Maxwell calculated the distribution of the velocities for a mechanical system such as we have assumed, if a fixed state were established. The expression can only be deduced in a very complicated manner, and has the form

$$y = \frac{4}{\sqrt{\pi}} . x^2 . e^{-x^2},$$

where y represents the probability that a molecule has the velocity x, if the most probable velocity is put equal to unity: π is the ratio of the circumference of a circle to its diameter, and e the base of the natural logarithms.

Mean Free Path.—From these considerations we can picture to ourselves somewhat more exactly the nature of a gas according to the kinetic hypothesis. The molecules are moving in all directions with very different velocities, and are continually encountering each other. We must for given conditions assume a mean free path which the molecule pursues undisturbed before it comes in contact with another. The molecules will evidently encounter one another all the more seldom the farther apart they are, and all the more frequently the larger their cross section. The mean free path L is thus directly proportional to the space allotted to each molecule, *i.e.* to $\frac{1}{n}$, if we designate by n the number of molecules in unit volume. It is further inversely proportional to the cross section ζ^2 of the molecules, if we understand by ζ the distance closer than which the centres of gravity of two molecules cannot approach. The exact expression is given by O. E. Meyer in the form

$$L = \frac{1}{\pi\sqrt{2} \,.\, n\zeta^2}.$$

ζ and n are both unknown, but from the phenomenon which led us to the question of the free path, viz. from the velocity with which one gas penetrates into another, the velocity of diffusion, we may draw conclusions as to their magnitude. The theory of these processes, as well as of the nearly related phenomena of gaseous friction and conduction of heat, is still by no means completely worked out, in spite of many efforts in this direction; yet we have got so far that the values of the free paths determined in different ways agree pretty well with each other. They are extremely small, in the case of air, for example, 10^{-5} cm., which is beyond the range of microscopic visibility.

Molecular Sizes.—When L has been determined, then, as may be seen from the equation, we are in a position to calculate $n\zeta^2$, the sum of the cross sections of all the molecules contained in unit volume. In this way we find that these cross sections amount to more than 1·5 sq. metres in 1 ccm. of air. This comes from the enormous number and small size of the molecules, for the more finely a mass of given density is divided the larger will be the total cross section of its particles.

One other datum is required before we can estimate the dimensions of the melecules. This is found by determining the total space occupied by the molecules.

If the molecules in a given mass of gas take up a measurable part of the space, this circumstance must have an influence on the validity of Boyle's law. For example, if the diameter of a molecule moving at right angles to two parallel walls of a cube be a hundredth part of the distance between them, the number of encounters will evidently be greater than if the molecule possessed no extension, for the molecule has each time to traverse, not the whole distance between the walls, but that distance minus its own diameter. The pressure will therefore, on account of this circumstance, increase more rapidly with decreasing volume than Boyle's law requires.

A correction for this may be easily introduced. If b be the space occupied by the molecules, then Boyle's law does not apply to the whole volume v of the gas, but to the space not occupied by the substance of the molecules, $v - b$ (*cf.* p. 47), and instead of the equation $pv = RT$ we get

$$p(v - b) = RT.$$

This correction b is of all the greater importance the smaller the volume is in which the gas is confined, and therefore can only be accurately observed at high pressures. It explains the irregularities which Regnault observed in the case of hydrogen, and which, according to the researches of Natterer and Amagat, appear in all strongly compressed gases (p. 47). In this way Budde (1874) calculated that for hydrogen, for instance, $b = \cdot 00062$ at a pressure of 76 cm. of mercury. Van der Waals then showed that, on the assumption of the kinetic theory, b is not to be taken as the molecular volume, but as four times the molecular volume, because of the motion of the molecules.

Now the total cross section of the hydrogen molecules in a cubic centimetre at 76 cm. pressure, according to the calculations given above (p. 508), amounts to 9500 sq. cm. If we call x the side of a molecule supposed cubical in form, 9500x must be equal to the total volume of the molecules, *i.e.* $\cdot 25 \times \cdot 00062$ ccm., whence $x = 1{\cdot}6 \times 10^{-8}$ cm.

The numbers obtained for other gases are very similar; they are usually a little smaller, but are generally independent of the atomic weight and the complexity of the substance. As these values are still very uncertain, they need not be given here. Still, the "dimensions of molecules" thus found have a physical significance quite apart from the kinetic theory. They are the dimensions below which the properties of the substance become different from those exhibited by the quantities which we are accustomed to deal with. They have been already discussed in this connexion (p. 83).

Number of Molecules.—From the molecular dimensions we can at once deduce the number of molecules in a mol, which, according to Avogadro's rule, is independent of the nature of the gas. The volume of a molecule, supposed to be cubical, and with a side of $1{\cdot}6 \times 10^{-8}$, is $4{\cdot}1 \times 10^{-24}$ ccm. As 1 ccm. of hydrogen has a molecular space of $\cdot 25 \times \cdot 00062$ ccm., that of 1 mol of hydrogen is 22400 times as great, as this is the volume of 1 mol of hydrogen (and of any other gas) at normal temperature and pressure. From this the molecular space of 1 mol of hydrogen is 3·47 ccm., and this divided by the above volume of a single molecule, gives the number of molecules in one mol as $\cdot 85 \times 10^{24}$, or in round numbers 10^{24}.

Calculations of this fundamental value of the kinetic theory, based on various other data, yield results which are a little higher or a little lower than this. The most probable value is $\cdot 71 \times 10^{24}$ (Perrin, 1908).

The Kinetic Theory of Liquids and Solids.—While the kinetic theory of gases has led to a very remarkable series of conclusions, the later confirmation of which has given us some confidence in its expediency, the development of a corresponding theory of the two other states of aggregation is still in its infancy, though hopeful beginnings have been made. The statement must suffice that mechanical reasons lead to the radical assumption that the mean kinetic energy of a molecule is independent of the state of aggregation, and is the same as that of a gas at the same temperature. The molecules of the same substance, therefore, move at the same temperature with the same velocity, whatever be the state of aggregation; only the nature of their paths is different.

The dominant factor in the case of liquids is the internal pressure (p. 81) which is merely a correction factor in the gas equation, but here conditions the volume proper of liquids, really independently of the external pressure. It also governs the phenomena of surface energy, of compressibility, thermal expansion, etc.

While the molecular motion in liquids must be assumed to be uniform in all directions, since they are isotropic in every property, crystalline solids exhibit ordered anisotropism, *i.e.* suitable properties are functions of the direction in accordance with the general laws of symmetry, which find their highest expression in the crystal form. Hence the assumption that the molecules have different properties in different directions, and that in crystals they are arranged either parallel to each other or at least in congruent relative positions (*e.g.* alternately perpendicular to each other), so giving rise to anisotropism.

The immediate conclusion from this, that the form of the molecule, indicated by the chemical constitution, must find expression in the crystal form, has not yet led to any simple general results, in spite of the attention which has recently been devoted to the idea; in certain special cases, however, some relations of this kind have been recognised.

BOOK VI

PHOTOCHEMISTRY

CHAPTER XXIV

RADIANT ENERGY

General.—Were it not that the available amount of free energy is continually replenished from the sun, it is safe to say that activity on the earth would long ago have been at a minimum, in virtue of the general dissipation of free energy, which constantly equalises differences of intensity wherever they exist. The sun sends forth into space unceasingly an enormous stream of energy, of which the earth receives only a very small fraction, namely, that which corresponds to its visual angle from the sun. By far the greater part of this again is dissipated without performing any definite work, as it merely keeps up the mean temperature of the earth's surface in spite of its radiation into space, and only an exceedingly small part of it is stored up by plants in the shape of chemical energy. On this fraction of a fraction of the sun's radiation live men, animals, and plants, the inhabitants of the earth and sea.

The energy which we (and the other planets) obtain from the sun in this way, is known as radiant energy. Light is a relatively narrow section of the many forms of radiant energy, viz. the part which can produce certain chemical processes in our eyes, and thus gives rise to light perception. From the physiological point of view, light (as a sensation) is first of all a transformation product of radiant energy. Another very frequent transformation product is heat, and this has given rise to the name radiant heat. But this is no more justifiable than it would be to give heat obtained from the transformation of kinetic energy the name of flying heat.

Radiant energy is known to us almost entirely from its transformation products, for it is the most immaterial of all the kinds of energy, *i.e.* it is practically unconnected with the spatial systems, within which we encounter mass and weight, and which we therefore call matter. It moves freely through space without any observable material carrier. Taking into account our usual habit of thought, according to which energy cannot be imagined without some carrier, a hypothetical carrier has been introduced under the name of the ether. It makes no actual difference whether the properties of the ether are ascribed to space itself, or to a special, space-filling something. For the latter can never be proved, but only the presence of energy in the space; for this reason it can never make any actual difference whether the properties of these spatially distributed energies are put down to the space itself or to a "carrier" present at the same place. For even if we accept the proof of the spatial heterogeneity of substances, or of their atomic structure, as satisfactory (as has been done above), this means neither more nor less than the substitution of rhythmic differences instead of a continuous arrangement in space, of those energies, the coexistence of which in space produces the particular properties of mass, weight, chemical nature, etc.; the rhythmic differences are of such a kind that the energy in question has a much greater concentration in certain points than in adjacent points. In other words, the energetic conception is not in contradiction to the atomic conception; the latter, on the contrary, must fulfil all the requirements of energetics, if it is to develop its particular conceptions. A grained or atomic structure of the ether, *i.e.* the space in which radiant energy acts, is not necessitated as yet by any known experimental fact. But, on the other hand, it is now practically certain that the energy of radiation is electromagnetic in nature, and it has been shown that electrical energy is very probably grained, or discontinuous in nature, like mechanical energy. To a great extent electrical phenomena can be referred to the action of electrical elementary particles, the electrons.

Thus radiant energy is very probably not an absolutely distinct kind of energy, the only connexion of which with other forms is their mutual transformation, but rather a special form of activity of electromagnetic energy, as sound is a special manifestation of kinetic energy and volume or elastic energy. The very special forms of this activity and its enormous importance in the economy of the earth, and of the whole known universe, fully justify their special treatment, just as heat is treated as an independent branch of science, and not as a separate division of mechanics, which from what has been already stated (p. 485) is quite justifiable on scientific grounds.

The Properties of Radiant Energy.—As radiant energy represents no specific kind of energy, it has not the properties of one, in particular it has not the characteristic factors of capacity and intensity. With this is connected the fact that it can neither be concentrated nor isolated, but must be treated in dynamic equilibrium with its surroundings, for it is formed and transformed automatically.

That it really is an energy is proved by its transformations. A radiating object loses energy, when it is doing nothing else but radiate; energy is formed when radiations are absorbed. It travels through space with very great, but not infinite, velocity, the rate being 3×10^{10} cm. per second, when no other kinds of energy are present. If they are present, especially if substances are present in the space, the propagation seems to be retarded.

If the radiation is absorbed by some obstacle, and is transformed into another kind of energy, the absorbing object experiences a pressure which is equal to the specific density of the radiant energy, *i.e.* to the energy in unit space. The direction of this pressure is the same as that of the radiation. This results directly from the fact that a pressure is equal to an energy divided by a volume. The pressure is greater if the absorption, *i.e.* the transformation of the radiation, is incomplete, and is doubled if the object completely reflects the radiation, as then the same space is filled with radiant energy of opposite direction. In spite of its extraordinary smallness, it has been found possible to measure this pressure (Lebedeff, 1901). It is so small because the space filled by radiation is very large in comparison with the amount of energy emitted in the interval, the velocity of propagation being so high. By way of illustration we may calculate the pressure of sunlight. The sun's radiation to the earth's surface develops about ·03 cal. *i.e.* $1{\cdot}4 \times 10^6$ erg. per sq. cm. per second, and fills a cylinder of 1 sq. cm. cross-section and 3×10^{10} cm. length. The pressure is then $\cdot 5 \times 10^{-4}$ absolute units, or, as one atmosphere is about 10^6 units, $\cdot 5 \times 10^{-10}$ atmospheres, equivalent to one two-millionths millimetre of water. While this is without any appreciable influence so far as ordinary mechanical phenomena are concerned, it is not so when the objects are very small, for the pressure on unit weight of a powder or mist subjected to radiation is a function of the specific cross-section, which, like the specific surface (p. 474) increases with the division. The significance of this from the point of view of cosmic processes has been clearly stated by Arrhenius (1900).

Beside the characteristic of a definite velocity of propagation, radiant energy has those of definite periods and wave-lengths. It is possible to resolve any radiation into a limited or unlimited number of individual radiations, each one of which has an absolutely fixed time period. The path of this radiation is divided into layers, in which the same difference is repeated. The thickness of these layers is called the wave-length of the radiation, and the number of periods in a second is called its oscillation frequency. The following relation holds between the wave-length l, the oscillation frequency n, and the velocity of light c:—$nl = c$, *i.e.* the number of oscillations in a second, put together lengthwise, gives the distance traversed by the radiation. The wave-lengths of some kinds of light in common use are given on p. 227.

Relation to Chemical Energy.—The importance of radiant energy for the subject of this book lies in the mutual transformation between it and chemical energy. Consideration of the energy used by living organisms, and of that available for technical purposes, at once shows that chemical energy is the most important of all. Further inquiry shows us the source of this energy, the radiation from the sun to the earth's surface. There it passes mainly into heat, and indirectly into the mechanical energy of meteorological processes, seen in the movement of air and water. Another more important portion of the radiated energy assumes through the instrumentality of plants the permanent form of chemical energy.

Through the action of sunlight there takes place in plants a series of important chemical processes, the details of which are mostly unknown to us, but their result is that the carbon dioxide of the atmosphere is decomposed into oxygen, which escapes, and compounds of carbon, starch in particular, which remain. As the heat of the combustion of starch into carbon dioxide and water is 17·24 kj. per gram, this amount of energy is necessary in order to form starch from the carbon dioxide and water at the disposal of the plants, and is supplied entirely by the radiant energy from the sun, for without sunlight plants are unable to effect the reduction of the carbon dioxide.

We see at once how this process affords us energy in a much more useful form than the meteorological processes, and in reality the portion supplied by the latter to drive wind-mills or water-wheels is very small compared to that stored up for us by the action of living plants. All fuel has this origin, and the animal organism can satisfy its requirements for energy in no other way than at the cost of the energy stored up in the vegetable world.

As the store of fossil fuel is not boundless, and cannot be renewed, the important question arises, what will become of our civilisation, when it is all used up. The answer is firstly that the above-mentioned meteorological energy in the form of rivers and water-falls is being much more fully utilised, since a way has been found of converting it into electrical energy. For the more distant future, the ideal is to convert radiant energy from the sun directly into electrical energy. As green plants, even under the most favourable circumstances, store up only 1/150 of the sun's radiation, there is plenty of room for improvement.

Image Formation by Radiant Energy.—Another and very important peculiarity of radiant energy is the extreme delicacy of its distribution in space. In striking contrast to heat which clings to matter and is continually subjected to a process of obliteration or diffusion, radiant energy retains in the minutest particular all differences in position originally imparted to it, even after it has moved millions of miles through space.

On this property depends in the first instance our power of seeing, which, to use Herschel's phrase, endows us more than any other with the attribute of omnipresence. The numberless minute differences possessed by radiant energy when it leaves matter, generate in the retina corresponding chemical changes, which give us a more faithful and more complete conception of the external world than is given by any other sense. This same property has also acquired technical importance: in photography, processes of quite comparable character are excited on a plate sensitive to light, which render possible the permanent preservation of an exact record of momentary states and phenomena.

Early History.—Photochemistry, then, like thermochemistry, was first developed round physiological and technical problems, the commencement in both cases being made about the same time. Priestley in 1772 made the observation that green plants in sunlight improve air vitiated by breathing; Senebier and Ingenhouss thereupon recognised that the process consisted in a decomposition of carbon dioxide with elimination of oxygen. The important part played by this in nature was, however, first appreciated at its true value by Liebig (1840), and J. R. Mayer (1842).

The oldest observations on light-pictures obtained with silver chloride were made by J. H. Schultze (1727), but remained isolated. The power of different rays to exert different actions on a sensitive substance was recognised by Scheele (1777), who first photographed the spectrum. Ritter discovered in 1801 that the chemical action extends even beyond the visible spectrum. Wollaston then took advantage of the blackening of silver chloride to copy silhouettes. Photography proper commences with Daguerre (1838), who discovered the development of light-pictures, on which rests the possibility of retaining the pictures of the camera obscura, and of photographing with great rapidity. The principle of it is that extremely feeble photochemical actions, themselves unable to effect any visible alteration on the sensitive surface, may afterwards have their effect rendered apparent by suitable treatment of the surface, and thus be converted into a picture. Although the means of arriving at this result have greatly changed since Daguerre's time, the principle still remains the same.

Emission and Absorption.—Although the mutual transformations between chemical and radiant energy form by far the most important part of our present considerations, some of the others must be dealt with in outline at least, as they have a bearing upon the chemical question.

Radiant energy is most easily obtained from heat, and it is known that a heated body is continually losing radiant energy, the amount of which depends on its surface, its temperature and the nature of the surrounding space. This is so general that radiant energy used to be called radiant heat. As it has none of the special properties of heat, and its formation is not exclusively confined to heat, this name is to be rejected as one-sided and fallacious.

If objects of different temperature are brought into a given space, they do not require to touch each other in order to equalise the temperatures; this can take place by radiation. There is, consequently, a very important relation, which was stated by Kirchhoff (1859). Let us suppose, for the sake of simplicity, two equal surfaces of different temperature and of different nature placed opposite to each other in such a manner that their radiations can reach only each other; an interchange of energy will take place, and at last the two objects will be at the same temperature. This must be so, according to the second law, since what is in equilibrium (as regards temperature) in one way, by radiation, must be so in all other ways, therefore by direct contact.

In this equilibrium the radiation absorbed by each surface is exactly balanced by the radiation sent out from it. If the amount of energy radiated in one second from the first surface, or the emission coefficient is A, this will be only in part absorbed by the second surface; we denote this fraction by bA, where b is the absorption coefficient of the second surface. The part $(1-b)A$ returns to the first surface and is absorbed by it. The first surface loses therefore bA. Further the second surface radiates B to the first surface, of which aB is absorbed: this is the actual loss of the second surface, the rest returns to it. The total energy lost by the first surface is $bA-aB$ and by the second $aB-bA$. Now, in equilibrium, *i.e.* at the same temperature, the two losses become zero, from which we have $bA=aB$ or $A/a=B/b$, *i.e.* the ratio between the coefficients of absorption and emission is the same for all substances, when they are at the same temperature.

As the temperatures equalised by means of radiation remain so when the simple conditions mentioned above are replaced by any others, it follows that the rule must apply to all kinds of surfaces and all kinds of rays. In particular, it is out of the question that only the total absorption and emission are proportional; the ratio must be the same for every single kind of ray (distinguished by its period and eventually by its plane of vibration).

If, therefore, an object can emit any particular rays in abundance, it necessarily has the power of absorbing the same rays in equal abundance from other objects. Conversely, if a surface could reject all incident rays, it would not be in a position to send out any rays.

We can imagine as a limiting case a body which absorbs all the incident rays without reflecting any of them; its absorption coefficient would be unity. If this be the first body, a would = 1 and S = B/b, where S is the emission coefficient in this particular instance. Such a body is called black; the equation indicates that the emission of a given body B is always smaller than that of a black body in the ratio of its absorption coefficient b. In other words, the radiation of a given body is obtained by multiplying the radiation of a black body by the absorption coefficient of the body.

The Temperature Law of Radiation.—The radiation of a black body is thus an extremely important fundamental magnitude. It depends on the temperature, and increases as the fourth power of the absolute temperature (Stefan, 1879; Boltzmann, 1884). The amount of energy radiated in one second by one square centimetre is expressed by the formula:

$$S = 5{\cdot}32 \times 10^{-5} T^4 \text{ erg.}$$

As a black body in this sense is only an abstraction, the question arises, how it can be experimentally realised. The answer is that a small opening in a space, the walls of which consist of any desired material at the given temperatures, acts as a black surface of the size of the opening. The proof of this is that a radiation penetrating into such a space will at last be completely absorbed in consequence of the numerous reflections from the partially absorbent walls, before any part of it finds a way out through the opening. Such a space has, therefore, the absorption coefficient 1, and consequently it has the emission of a black blody (Kirchhoff, 1859; Lummer and Pringsheim, 1900).

The amount of radiation of individual periods is also a general function of temperature. Recent investigations have led to a general result, but details cannot be given here.

Spectrum Analysis.—An important relation between radiant energy and material substances is that the production and transformation of radiation on them present regularities in respect to periods. In many instances, only radiation of fixed period is evolved or transformed, and this indicates the periodic character of the substance concerned. Conversely, we may conclude, from the absence of specific emissions or absorptions, that these periodic properties are not present, or, what amounts to the same thing, that the properties in question have all the possible periods within the present limits.

Owing to the direct connexion between emission and absorption, there are two methods of estimating these periods: either the radiation which the substance emits is examined, or a radiation containing all possible periods is sent through the substance, and the periods which are absorbed are ascertained. Both methods are in use; they have given the same results in cases where both could be applied to the same substance under the same conditions.

The simplest behaviour is that of gases. When gases are made luminous by raising their temperature or in some other way (*e.g.* by means of electrical discharges), they emit rays of definite period, which depends on their chemical nature, but is within very wide limits independent of the temperature (Bunsen and Kirchhoff, 1859). The periods are not restricted to a single one for each substance; the number of periods for any substance is extremely great when the investigation is extended over a sufficiently wide range of temperature; but they are situated in isolated positions over wide tracts of the periods present, and all the intermediate periods are absent.

To render them visible together, use is made of the dispersion produced by a prism of glass or of some other transparent substance, or of diffraction at a grating. The light is placed behind a narrow slit, which is at the focus of a condenser; the parallel beam so obtained is sent through the prism. The light is refracted to a different extent according to its period, and when the parallel beam is viewed through a telescope, focussed for infinity, there appear, instead of the simple image of the slit, as many distinct images side by side as there are different kinds of rays in the source of light. The light of incandescent solids and liquids usually contains rays of all periods. The image then appears as a continuous band of light, in which all colours from red to violet are present in continuous succession. If only some periods are present, there appears, in place of the uninterrupted band, a series of sharply defined lines of the width of the slit. These images, in which the rays are arranged in order of their periods, are called spectra, and the apparatus is a spectroscope.

While there is no simple connexion between the periods and the deviation of the rays in the spectrum produced by refraction in a prism, there is such a relation in the spectra produced by a diffraction grating. The production of these spectra is explained in the text-books of Physics; all that need be said is that the angle of deviation is proportional to the wave-length of the refracted light. Consequently diffraction spectra are much simpler theoretically. At the same time the dispersion of the different rays is much greater, so that the diffraction grating permits of a much more extensive analysis of light than does a prism spectroscope. If the formation of the image and the dispersion are produced in one apparatus by the use of a grating ruled on a concave mirror of large radius, a very perfect spectroscope is obtained.

To obtain the spectra of luminous gases and vapours, they are heated in a suitable manner, and the light analysed by means of a spectroscope. The heating is most simply effected in the almost non-luminous flame of a Bunsen burner, into which the substance which gives off the desired gas by vaporisation or decomposition is introduced. The temperatures of the flame, however, are not high enough to make all gases luminous. The electric discharge is used for higher temperatures. An electric arc is produced between two carbon poles, and the substance to be vaporised is placed on the positive carbon, as it is the hotter. The simplest arrangement is to use a hollow carbon tube, which is filled with the substance; but for short experiments the substance may be placed in the crater formed on the positive carbon.

Still higher temperatures are obtained if electric sparks are passed between the electrodes, which consist of or contain the substance under investigation. If the substance is a gas at ordinary temperature, the electrodes are surrounded with the gas.

In all these cases the spectrum is that of all the other substances present, as well as of the substance investigated. It is necessary, by means of preliminary investigations, to find out to what substances the different lines belong. This is often a very difficult matter, for mere traces of impurities often give well-marked spectra, without any other indication of their presence.

Properties of Spectra.—The general laws, which have been discovered for the spectra of different substances, may be summarised as follows:

A given spectrum always belongs to a given substance; different substances never have the same spectrum.

The converse of this law does not appear to be true, for numerous cases are known in which the same substance gives different spectra. At first these differences were ascribed to different molecular states of the substance. This explanation is untenable, for there are several substances which give different spectra, and yet are only known in one state. Argon affords the most striking illustration of this. According to our present knowledge it must be regarded as a monatomic gas, which forms no compounds, and yet shows at least three essentially different spectra.

The cause of this formation of different spectra seems to be mainly the difference of temperature. The temperature differences necessary to bring about the change vary very much.

The spectra of compounds are different from the spectra of their elements.

While the spectra of different substances, which are present together, are quite independent of each other, *i.e.* are perfectly additive (on this depends the great value of spectrum analysis, as no previous separation of the substances is necessary), no relation between the spectra of elements and their compounds is known with certainty. This may be partly due to the difficulty of ascribing the compound spectrum to any definite substance, as so little is known with certainty about the compounds which are formed at high temperatures from any given elements.

There is a connexion between the absorption spectra of more complex compounds and the nature of the compound, as will be seen later.

The various lines of the same spectrum are related to each other in an ordered manner.

The general form of this connexion has not yet been established. In some cases the relation

$$n = A - B/m^2$$

holds, where n is the oscillation frequency, A and B are constants, and m is the series of whole numbers. This relation is satisfied with very close approximation by hydrogen. In the case of other elements, a term with c/m^4 has usually to be added; here, the lines of one and the same spectrum decompose into several different series with different values of the constants.

Similar elements show a similar form of spectrum.

A similarity in the spectra of the alkali metals was discovered by the first investigators, as the few lines developed in the Bunsen flame show an analogous structure; the oscillations of the corresponding lines for potassium, rubidium, and cæsium become slower as the combining weight of the element increases. Similar relations for the constants of the series mentioned above are found to hold for the much richer spectra of these elements in the electric arc. Similar analogies have also been found for the bivalent elements of the magnesium group.

Absorption Spectra.—Compounds cannot as a rule be rendered luminous by heat without decomposition; attention has, therefore, been mainly directed to their absorption spectra.

The relation between emission and absorption has been most accurately confirmed on gases. It gives rise to the reversal of the lines. If under the prevailing conditions a continuous spectrum is formed in the presence of the gas, dark lines appear in place of the bright lines of the luminous gas. This happens if the continuous spectrum is much more luminous than the single radiations. The light has then to pass through a layer of gas; it thus loses these rays by absorption, and the lower intensity of the radiations emitted by the gas causes them to appear as dark lines on the bright ground of the continuous spectrum. The brightest lines are in general most easily reversed, as they represent the places of strongest absorption.

The absorption spectra of liquids or of solutions are essentially different from those of gases; sharply defined lines, indicative of absorption in a quite narrow region, never occur. The absorptions are always more or less diffuse, and absorption bands, instead of lines, are the result.

Absorption in the visible spectrum, which leads to the phenomena of coloured substances, has because of its special interest been very fully investigated. On this account, our knowledge of the subject has remained one-sided, and this is reflected in the absence of general laws. It can only be stated generally that it is a strongly constitutive property. The simplest derivatives of the saturated hydrocarbons are transparent for most rays, and definite absorptions first occur when particular constitutions are present. Thus the presence of nitrogen and of double bonds are favourable for absorption; still more do the various groups of cyclic compounds form the storehouse of absorbing substances. In the simpler cases the absorption is chiefly in the ultra violet, and only under certain conditions does it extend to the visible spectrum.

Within cognate groups a few particular relations are known, in so far as the introduction of certain groups into a coloured compound displaces the absorption in a definite direction. Thus methyl or other alkyl radicals, and usually also the halogens, displace the bands towards the red end, while the amido group, and often also the nitro group, displace them towards the shorter rays. The extent to which they are displaced also depends on the constitution. These have been embodied in certain rules, which are of great technical importance, for they indicate how a given dye can be converted into one of some other desired tone.

The derivatives of fluorescein afford an illustration of this. It has an absorption band in the blue, and therefore appears yellow (by transmitted light). The introduction of chlorine, bromine or iodine displaces the band towards the green, and the displacement increases from chlorine to iodine. This causes the substance to appear red, and more purple red, as the band is displaced further towards the red end. This effect of the halogens differs according as the substitution takes place in the phthalic acid residue, or in the resorcinol residue; it is smaller in the former case.

Again, the absorption band of rosaniline, which is situated in the green, goes farther towards the orange and yellow when methyl or phenyl is introduced, and the resulting compounds are coloured violet and blue respectively.

Colour of Ions.—Only in one case does considerable alteration of a constituent give rise to no change in colour: in dilute solutions of salts. An investigation by Ostwald (1892) showed, for example, that the five sharply defined absorption bands of permanganate solutions are in exactly the same position, whatever salt of permanganic acid is investigated. The explanation of this is found in the independent existence of ions, which implies that the properties of one ion are independent of those of other ions. As absorption phenomena are very sensitive to constitutive influences, this is a strong support for the theory of independent ions.

Unionised salts frequently differ in colour from their ions. Thus anhydrous cupric chloride is yellowish-brown, and cupric bromide is violet-black, while in dilute solutions they both possess the greenish-blue colour of cupric ion. It must be noticed that a difference is generally to be expected, but it is not necessarily present. In the complex salts of trivalent chromium we have compounds which show on the whole the same absorption, in spite of constitutive differences of composition. It has not yet been made out what are the constitutive conditions which produce so small an effect on absorption.

Electromagnetic Waves.—The region of absorption phenomena has lately been so widely extended that it now includes electromagnetic radiation.

When electrical oscillations are produced in a conductor, it sends out energy into the surrounding space, and this energy has the same properties, the velocity in particular, as the ordinary radiant energy known as light. If this radiation reaches electrical conductors it is absorbed with the formation of electrical currents, which again are transformed, in conformity with Joule's law, into heat according to the conductivity of the absorbing object. Investigation of these phenomena has shown that all the essential properties of radiant energy are exhibited by them. This has led to the development of the idea that radiant energy consists essentially of electromagnetic oscillations, and the electromagnetic theory of light based on this idea has actually proved adequate to represent the facts in a satisfactory manner. It must be admitted at once that the energy obtained from electromagnetic oscillations shows absolutely no electrical or magnetic properties, so long as it is in the radiant condition. It has lately been shown that a magnetic field exerts a direct influence on light oscillations in the field; light of definite oscillation frequency is resolved into two rays of slightly different frequency. This was predicted by Lorentz from the electromagnetic theory of light, and was subsequently proved experimentally by Zeemann (1904).

The inclusion of electromagnetic rays has enormously enlarged the region of radiant energy, for rays of any wave-length can be produced in this manner. The absorption of electromagnetic rays by different compounds is subject to constitutive influences similar to those already observed in the region of visible light (Drude, 1897). Details cannot be given, but it may be mentioned that hydroxyl compounds have shown the power of absorbing rays of 10 to 20 cm. wave length.

Conclusion as to the Nature of Substances.—The theoretical importance of the phenomena of emission and absorption is that they enable us to recognise the presence of periodic properties in the radiating or absorbing substances; these periods must either be identical with the periods of the radiation concerned or stand in a multiple relation to them. The periods may either be periods in time (atomic oscillations) or in space (atomic sizes); probability is in favour of the latter kind. What their nature is, is as yet unknown. Formerly, when light was regarded as the oscillation of a hypothetical elastic medium, the ether, it was conceived to be the oscillation of the atoms: the difficulties which this entailed were, on the one hand, that the periods are in the highest degree independent of the temperature, and therefore of the amplitude of the oscillation, and, on the other hand, that the different rays of the same spectrum should stand in the same relation to one another as the overtones of a vibrating body, which cannot be reconciled with the facts. At present light is regarded as an electromagnetic oscillation, and a corresponding electrical nature (resonance of conductors) is assumed for substances which absorb. Investigations along this line have led to some very remarkable results, but not to such as can find mention here.

Transformations.—Radiant energy undergoes transformation on absorption. Heat is the chief product, but there are also cases where other forms, and especially chemical energy, result. The latter are of special interest for us.

Conversely, chemical energy is frequently transformed into radiant energy. We must not think in this connexion of the fact that in most lamps (with the exception of electric lamps) chemical processes supply the source of light energy, for these are chiefly secondary phenomena, the chemical energy being transformed into heat, a small portion of which passes into light owing to temperature radiation. But such phenomena as the luminosity of phosphorus, of many fungi (on decaying wood and occasionally on flesh), of the glow worm, etc., are examples. These are not cases of ordinary temperature luminosity, for they are all under 50°, but of the direct transformation of chemical energy into radiant energy. The number of cases of "chemiluminescence" has been largely increased in recent years (W. Trautz).

Accordingly, Photochemistry, or the theory of the mutual transformations of radiant and chemical energy, should be divided into two parts, one dealing with the formation of chemical energy from radiant energy, and the other with the reverse process. But the former alone has been fairly well developed. Towards the latter, only a few observations of the kind just mentioned have been made, and the first rudiments of scientific treatment of the subject scarcely exist. We have consequently to deal exclusively with the first part.

CHAPTER XXV

THE CHEMICAL ACTION OF LIGHT

General.—Photochemical phenomena consist in the chemical changes which a system undergoes when radiant energy enters it. But before any action can occur, the energy must be transformed; absorption thus necessarily precedes all photochemical action.

These actions can be divided into two main groups. There is in the one case, absorption of energy due to the absorbed radiation, resulting in the formation of new chemical products, which contain more energy (free and combined) than the original material. The best known and most important example of this is the reduction of carbonic acid by green plants, resulting in the formation of starch and similar reduction products on the one hand, and the liberation of free oxygen on the other.

In the second group light acts as a catalyser, accelerating reactions which are already proceeding at a slow rate, and which, therefore, are accompanied by a diminution of free energy. The union of hydrogen and chlorine is the best known example of this class; as a large amount of energy is liberated during the reaction, it takes place spontaneously. But in the dark the rate is very slow, and is increased by light proportionally to its intensity.

It is not impossible that the first effect in the catalytic actions is to increase the chemical potential of one or some of the reacting substances as a result of absorption of radiant energy; this increase then accelerates the reaction. This view is supported by the proportionality between the acceleration and the intensity of the light, which would not be expected if the process were simply a starting of the chemical action. The latter process must occur, when, as in the explosion of chlorine and hydrogen in sunlight, the reaction, once started, proceeds rapidly to completion, owing to the high temperature produced (see below).

Formerly the study of photochemical processes was restricted to the second type, but recently a number of reactions of the first type have been discovered. In them radiation acts as a form of energy participating in the equilibrium (Luther, 1902).

Sensitiveness to light is to be expected of all substances which can absorb, and the difference between one substance and another becomes merely a question of degree. In fact, the list of substances which are changed by light is very large, and is constantly being added to.

To obtain some idea of the way in which the chemical condition of a system may be changed by means of radiations, we may suppose a number of different absorbing substances to be brought into a space of constant temperature. They will assume this constant temperature. A continuous radiation is then directed into the space, it is absorbed to different extents by the substances, and the absorbed rays are changed into heat; the substances thus assume different temperatures, which are given by the ratio of the absorption of the rays to the emission at the resulting temperatures.[1] Consequently their behaviour towards one another will not be the same as in the dark, and they will readjust themselves to the new conditions.

Laws of Photochemical Action.—Only a small number of photochemical actions have been investigated quantitatively. The reaction between equal volumes of chlorine and hydrogen, first discovered by Berthollet, has been more fully investigated than any other. They unite to form hydrogen chloride on exposure to radiations. If intense light is allowed to act on moderate quantities of the gases, the union takes place in a few moments with an explosion; if the light is moderated, the reaction takes place in a regular and slow manner. Under the latter conditions it can be used to make measurements.

Chlorine and hydrogen unite also in the dark, if the temperature is raised high enough, and locally raising the temperature of a small part, *e.g.* by means of an electric spark, will cause any volume of the gas, however large, to unite with explosive violence. The cause of this is the large amount of heat evolved by the reaction itself. This raises the temperature, in the vicinity where the first combination occurred, to such a degree that rapid combination takes place there also, and thus the reaction is propagated through the entire mass. The same consideration applies to the combination under the influence of light. If the heat produced is carried away so slowly that the temperature becomes high enough to cause rapid union, combination becomes explosive. If the exposure to light takes place under conditions which preclude such a rise of temperature (it is better to avoid any appreciable rise), combination proceeds in a continuous and measurable manner.

The measurement of the chemical action of light on the hydrogen and chlorine mixture is based on the circumstance that the hydrogen

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[1] Kirchhoff's law (p. 516) cannot be applied in such a case, because we are not dealing here with an equilibrium between mutually opposite radiations, for which this law holds, but with the action of an independent external source of radiation.

chloride is instantly absorbed by water, while the absorption of the components is slight. The mixture is illuminated in contact with water (saturated with chlorine and hydrogen under the experimental conditions) in an apparatus which permits the measurement of the decrease in volume; the latter is a measure of the amount of combination.

An apparatus for this purpose was first constructed by Draper (1842); Bunsen and Roscoe later (1862) devised a more perfect form.

The principal part of the apparatus is shown in Fig. 66. The mixture of chlorine and hydrogen prepared in exactly the right proportions by electrolysis is led from h through the "insolation" chamber i, which is made of thin glass blown in the form of a flat circular box, and contains water in its blackened lower half. It is connected by a ground-glass joint with the measuring-tube k, which ends in the chamber l, also filled with water.

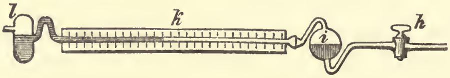

FIG. 66.

If light falls on the upper portion of i, hydrogen chloride is formed, and this is immediately absorbed by the water. A diminution of volume is the result, and the water lk in the tube moves towards i; the distance the water has moved is read off on the scale, and is a measure of the chemical action of the light.

By this arrangement the product of the action of light, hydrogen chloride, is removed as soon as it is formed; and the apparatus remains in the same condition throughout the experiment.

With this apparatus, Draper, and subsequently Bunsen and Roscoe established the fundamental law of photochemical action, viz. that the action of light is proportional to its intensity.

Draper (1842) projected by means of a large lens an image of a uniformly illuminated white surface on to his apparatus, which measured the action of light by the amount of hydrogen chloride formed from a mixture of chlorine and hydrogen. The result he obtained was that, when the lens was partially covered by sectors of known angle, the action was proportional to the uncovered surface of the lens. Hankel (1862) and Bunsen and Roscoe confirmed this law.

In this form the law refers to the action of a uniform radiation in unit time. If the radiation is variable, the effect in each fraction of the time is proportional to the radiation at that particular moment. If, then, each intensity of radiation is multiplied by the time of its duration, the sum of the products is, according to the fundamental law, proportional to the total chemical effect. The sum of the products, however, is the total energy of the radiation which has acted during the whole time; the fundamental law can thus be put in the form: in a given system the energy of the radiation which is converted to chemical uses is a constant fraction of the total energy of the radiation.

It is difficult to test the accuracy of this law, for the supposition that the nature of the system undergoes no change during the radiation can never be strictly satisfied. In Bunsen's apparatus, for instance, the hydrogen chloride is not instantly absorbed, but merely very rapidly; there is thus always some hydrogen chloride in the apparatus during the work, and the amount is easily seen to be proportional to the velocity of the reaction, and not constant. Similar objections can be made in all such cases.

Further, it was found by Bunsen and Roscoe that the union of hydrogen and chlorine is preceded by certain processes which decrease the velocity of reaction, so that a constant velocity is not reached until after prolonged exposure to a constant source of light. These phenomena of "photochemical induction" are also found in other cases; they are probably due to very small traces of oxygen, which, in contrast with chlorine, has been found usually to retard photochemical actions. The oxygen seems to be used up during the first stages of the reaction, after which the reaction proceeds normally.

The next question is, What fraction of the total amount of radiant energy is utilised in chemical action in a mixture of chlorine and hydrogen? Bunsen and Roscoe obtained an answer in the following way:

A beam of light from a constant gas-jet was first passed through a cylinder filled with chlorine, and the loss by radiation to the chlorine (which warms the chlorine) measured. A cylinder of double the length, and filled with a mixture of equal volumes of chlorine and hydrogen, was then placed in the path of the beam. As hydrogen does not absorb rays to any measurable extent, the light on passing through the mixture should have been weakened to the same extent as in the chlorine alone, if it performed no other work in the second case than it did in the first. The weakening, however, was found to be perceptibly greater, so that the authors came to the following conclusion:—

"Of the rays from a gas-jet, which are absorbed by the mixture of hydrogen and chlorine, two-thirds serve to heat the gases, while the remaining third is spent in performing the work necessary to put the two gases into such a condition that they can enter into chemical combination."

Investigations into the active portion of light falling on a sensitive substance have shown that it is in general very small. According to Pfeffer $5{\cdot}4 \times 10^{-8}$ g. of starch is formed by a square centimetre of surface of an oleander leaf per second under the most favourable circumstances. The heat of combustion of this quantity is only $9{\cdot}2 \times 10^3$ erg., which consequently is also the energy spent by light in forming the starch. Now the radiant energy received by a square centimetre on a clear summer day is $1{\cdot}4 \times 10^6$ erg. per second; the plant, therefore, cannot use as much as the hundredth part of this for chemical purposes.

From this example we see that the fraction of radiant energy, which is used for chemical purposes, can vary to an extraordinary extent according to the circumstances. It can never exceed the total amount absorbed; but there appears to be no constant relation between the total absorption and the chemical absorption. No direct conclusions can be drawn as to the chemical sensitiveness to light from the general optical absorption.

General.—The laws of the chemical action of light are deduced from the fundamental law of photochemistry and the general laws of radiation. Thus the decrease in chemical action is inversely as the square of the distance from a source of light radiating in all directions, and when light passes through an absorbing medium, the amount absorbed increases geometrically as the thickness of the medium increases arithmetically.

Further proof that all the geometrical laws of radiant energy apply also to its photochemical action, is afforded by the fact that every objective optical phenomenon can be photographed.

These laws have been tested by various methods, especially by means of sensitive plates and papers, and the same results have always been obtained, independently of the nature of the material used.

The answer to the question, Which rays produce chemical action? is that it is determined by the period or the wave-length of the rays, there being for every sensitive system a maximum (or several) of action at definite periods. The circumstance that the most striking chemical effects of light have been observed in the case of substances whose chemical absorption lay in the blue, violet, and ultraviolet region, led to the view that the rays of short wave-length are the "chemical" rays. Later researches have shown that chemical effects can be produced by all the rays of the visible and invisible spectrum, and that it depends only on the nature of the substances what rays come into action. Measurements of the "chemical intensity of light" or of the "photochemical climate," which were formerly made so frequently, have no theoretical significance, as they only reproduce the temporary local variations in intensity of the rays which have a particularly strong effect on the actinometer employed.

No general connexion between photochemical sensitiveness and chemical nature has been made out. Since the region of chemical absorption must lie within that of optical absorption, we have to look among coloured substances for those which are sensitive to visible rays. A very slight degree of colour, however, is sufficient to confer very considerable sensitiveness, as is evident in the instance of the almost colourless silver halides.

Finally, oxidation and reduction processes seem to be particularly susceptible to radiant energy. Consequently almost all the salts of metals, which can form ions of more than one valency, are sensitive to light. This is very noticeable if other substances are present which can undergo reduction or oxidation, as the case may be.

Photography.—The method by which Daguerre first accomplished actual photography consists in exposing a plate of silver (or of thickly silvered copper) to the vapour of iodine, and then allowing the image in the camera obscura to act on the plate. After the action, which only requires a few seconds, the plate, on which no image is visible, is exposed to the vapour of gently heated mercury. The vapour condenses on the plate the more densely, the more strongly the light has acted at the spot in question. If the plate is looked at so that the bright places reflect little light to the eye, the parts where there is a deposit of mercury globules appear brighter than the background, proportionately to the thickness of the deposit.

The theory of this process is based on the fact that vapours condense in general more readily on rough than on smooth surfaces. Where the silver iodide has been acted upon by light it is partially decomposed, and thus a better surface is offered for the deposition of the mercury globules. We may perhaps have the additional circumstance that the separated silver has more affinity for the mercury than the undecomposed iodide has, and therefore condenses it more readily. From the researches undertaken after the acquirement of the knowledge of Daguerre's method, it has been proved that the slightest local alteration in the state of the surface of a polished sheet changes the manner in which vapours condense on it in the most remarkable way. It is a result of the influence of a foreign substance on the metastable limit.

Newer Processes.—Daguerre's method is now completely abandoned. It was first displaced by Scott Archer's collodion process. A solution of gun-cotton (cellulose nitrate) in ether and alcohol is made to dissolve certain iodine compounds (cadmium iodide, ammonium iodide, etc.). A glass plate is then coated with the solution, and after the greater part of the ether has evaporated, is dipped into a solution of silver nitrate. By this means a sensitive precipitate of silver iodide is formed in the coating of collodion.

If such a plate is now brought into the camera and exposed for the necessary length of time—a few seconds in daylight—no alteration in the yellowish-white coating is observed. An image only appears when the plate is immersed in a mixture of silver nitrate and a reducing liquid, *e.g.* a solution of pyrogallol or of ferrous sulphate. The silver which separates from this mixture deposits preferably on the places where the light has acted, and produces an image in which the silver deposit is proportional to the light-intensity. By treating this "developed" image with a solvent for silver iodide, *e.g.* potassium cyanide, the excess of iodide is removed and we have left a negative, with the light places opaque and the dark places transparent.

As the foundation of the theory of this process, we have the behaviour of supersaturated solutions in contact with nuclei. In the coating of the plate under the developer the image consists of metallic silver,[1] while the mixture of silver nitrate and reducing agent, *i.e.* the developer, represents a supersaturated solution of silver. The silver is deposited from the solution wherever nuclei of silver are present, and thus a visible image is produced. The development can be prolonged until the thickness of the deposit is sufficient for the required purpose. This can be done either on the fresh image in the silver iodide layer, or after "fixation," *i.e.* after the image has been freed from silver iodide by treatment with potassium cyanide solution.

The collodion process is now used only for a few purposes, and has been replaced almost entirely by silver bromide gelatine plates. They have, in addition to their greater sensitiveness to light, the very great advantage that they can be prepared an indefinitely long time before use without undergoing deterioration, whereas collodion plates must be used at once after dipping in the silver bath.

They are made by adding an ammoniacal silver solution to a warm solution of pure gelatine and potassium bromide; the bromide must be in slight excess. Silver bromide separates in the colloid state, and is at first insensitive. It becomes more sensitive on prolonged digestion at a slightly higher temperature, probably on account of incipient decomposition of the silver bromide, and after a definite time it is sufficiently "ripened." The mass is then allowed to solidify, and the potassium nitrate is washed out; the mass is then melted, poured out on to glass plates, and allowed to dry.

These plates are developed by means of strong reducing agents, such as potassium ferrous oxalate, or alkaline solutions of hydro-

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[1] Later experiments have made it certain that the undeveloped image in the collodion-silver iodide coating is not metallic silver, but a silver sub-iodide or a similar reduction product of silver iodide, since it is not destroyed by nitric acid, although it is destroyed by iodine. Important as this is in itself, it is of no consequence for the theory of development, since the sub-halides of silver immediately form metallic silver when they are acted on by developers, and this silver then plays the part mentioned above. The same consideration would apply if the primary image were a colloid solution of silver in excess of silver halide, since it has been proved that metallic amicrons are capable of development (p. 491).

quinone or other aromatic compound containing several hydroxyl groups. The silver bromide is reduced to silver mainly at the parts exposed to the light. Finally, the image is fixed by treating the plate with sodium thiosulphate, which removes the unchanged silver bromide.

The theory of this development is practically the same as the theory of the collodion process. Here, also, the action of the reducing agent on the silver bromide produces a supersaturated silver solution, which deposits the metal on the nuclei present.

Production of Positives.—This process, too, gives only negatives, *i.e.* the light places are opaque, and the dark ones are transparent. The processes of making positives from them are very numerous and widely different. Those most frequently employed depend upon the darkening of silver salts in the light, when they are in contact with organic substances. Under these conditions the silver salt is reduced to silver, in inverse proportion to the density of the negative, so that a correct picture is obtained. The excess of silver salt is dissolved out with sodium thiosulphate, and a silver image remains. As this silver is of an unpleasing brown colour, it is treated with a very dilute gold solution; by this means the silver of the image is partly replaced by gold, the bluish-violet colour of which, together with the brown of the silver, gives the well-known photographic purple tone.

The platinotype process utilises the reduction of ferric salts in light. Potassium ferric oxalate, to which potassium chloroplatinite has been added, is usually employed. After exposure to light, the image is treated with a solution of potassium oxalate, on which the ferrous salt produced at the reduced places precipitates metallic platinum from the platinum salt.

A large number of other processes are based on the reaction between chromates and organic adhesive substances, such as gum and gelatine. The chromic acid is reduced to chromic oxide on exposure to light, and the oxide forms an almost insoluble compound with the gum or gelatine. By this means a pigment, which has been ground up with the mixture, is fixed at the places acted on by light, and, on washing away the unchanged coating, we obtain a positive.

Several photographic printing processes have been based on this reaction. Asphalt has also been used for this purpose, as, on exposure to light, it loses its solubility in oil of turpentine. The details of these various methods cannot appropriately be given here.

A remarkable observation was made in 1874 by H. W. Vogel. Silver salts, and particularly the silver bromide of ordinary plates, are specially sensitive for rays of small wave-length, between blue and ultraviolet, while the yellowish-green rays have the most powerful effect on the eye, and for these the plates are not at all sensitive. In consequence of this, the gradations of light are changed in photographs; the darker blue and violet colours come out bright, while bright red and yellow tones are dark in the photograph.

This disadvantage can be overcome by adding traces of certain dyes, *e.g.* eosin or cyanin, to the silver bromide of the plates. The maximum of photochemical action is displaced to the side of greater wave-lengths, or new maxima occur in this region; the result is more correct gradation in the photograph.

The theory of this process has not been satisfactorily made out. The dye appears to form a compound with silver, which is sensitive to light; but it has not been shown to be of the same order of sensibility as silver bromide. It may possibly form a solid solution with the silver bromide, which has its total sensibility correspondingly displaced.

CHAPTER XXVI

CONDUCTION IN GASES AND RADIOACTIVITY

General.—Numerous series of phenomena of various kinds have been discovered and investigated in recent years, which are related to radiant energy, since they are concerned with kinds of energy which traverse space in straight lines and with a very great velocity. They are not in a state of vibration, by which the energy is propagated, the processes being rather of the type which Newton supposed to constitute the nature of light. In other words, small particles, the lower limit of which amounts to ·001 of the mass of a single hydrogen atom, are projected rectilinearly through space with velocities which approach that of light.

These small electrically charged quantities, which cannot apparently be further split up, are called Electrons, and an atomic structure is accordingly ascribed to "Electricity." Since the division relates to quantities of electricity, and not electrical energy, the assumption requires extension with respect to the potential of the quantity of electricity, which, according to the laws of electrostatics, depends on its space relationship.

An electrically charged sphere possesses a negative surface tension, in virtue of which it strives to increase its surface if possible. By what means the tendency to expansion is restrained in electrons, has apparently not yet been discussed.

There are both positive and negative particles of equal size. They are usually associated with ponderable atoms, but a number of facts leads to the conclusion that negative electrons occur alone without ponderable atoms, while isolated positive electrons are unknown. Kathode rays, in particular, which are formed by electrical discharges in gases at low pressures, consist of negative electrons possessing a very high velocity.

Gas Ions.—The experimental fact which has led to the development of these conceptions, is the electrical conductivity of gases. After the dissociation theory of liquid electrolytes had shown the value of the conception of ions in the classification of known facts and the discovery of new ones, it was natural to apply the same ideas to gaseous conductors. It was found necessary to make many extensive alterations before it became possible to represent the particular circumstances.

The chief difference is that in gases there is apparently no intrinsic cause (arising from their own nature) of ion formation, as there is in aqueous and other conducting solutions and in fused liquids. The conductivity is a result of external causes, *i.e.* the introduction of energy, and even while this cause is at work, still more when it ceases, a process of recombination is taking place which leads to the spontaneous disappearance of the ions, and consequently of the conductivity. Thus in any case the ionised part of the gas is extremely small, for when the attempt is made to increase it the recombination is also increased, and a limit is soon reached. The velocity of recombination shows it to be a reaction of the second order (p. 293).

The causes which produce these effects are very various. The one longest known is electrical discharges of all kinds. But numerous chemical processes have the same effect, *e.g.* violent combustion, the luminous oxidation of phosphorus in the cold; as have also the action of light, especially ultraviolet light, on many substances, particularly metals; also the heating of metals above 300°. Finally, the radioactive substances possess this power in such high degree that they were recognised and investigated by means of it. To summarise, it may be said that all kinds of concentrated energy (*i.e.* a large amount of which is condensed in small space and is therefore of high potential and can perform intensive work) possess the power of making gases conductors of electricity.

That this conductivity is due to the presence of individual electrically charged particles, the gas ions, follows from the fact that the cause of the conductivity has the properties of a fine dust. Filtration through cotton wool, even leading the gas through a zigzag narrow metal tube, washing it with water, and similar operations remove the conductivity, since they remove the conducting particles. The conductivity is also lost when the gas is brought between the oppositely charged plates of an electrical condenser, because the electrically charged particles travel to the plates. This is entirely due to the electrical charge on the particles.

In accordance with this, conduction in gases does not obey Ohm's law. In an electrolyte the quantity of electricity which the ions can collectively transport is very large in comparison with the quantity they must transport under the usual conditions of current and time, so that the current has no effect on the conductivity. We can readily perceive that a dilute electrolytic solution, placed in a thin layer between two electrodes, will soon be exhausted by the current, and that such a solution will not obey Ohm's law, *i.e.* the current strength will not be without influence on the resistance.

Such a condition is always present in gases, and it is only by the continuous application of the cause of ionisation and by the use of extremely small current-strengths that an approximation to Ohm's law is obtained. When an ionised gas is left to itself the spontaneous recombination of the ions is added to the loss of ions by conduction, and thus the deviations from Ohm's law become still greater.

On the other hand, with constant ionisation and stronger potentials another limit is reached, the current-strength then being independent of the potential. It is then only dependent on the productiveness of the source of ionisation, since under no circumstances can more electricity be transported than the ions are capable of transporting in the time.

These facts and their significance have been developed mainly by J. J. Thomson and his pupils (since 1894), to whom we owe the fundamental explanations of the subject.

Properties of Gas Ions.—These gas ions display none of the properties of atoms or molecules of the gases, in which they are produced and with which they might be identified. Their velocity of migration has been ascertained from their conductivity under different measurable conditions; it is found to be about ten times as great as for ions in electrolytes. There are no serious differences between ions produced in various gases, such as might be connected with the molar weight of the gas. It makes a much greater difference whether the gas is moist or dry during ionisation. The ions in hydrogen gas are alone different; their velocity is several times greater than those of other gases. It may be surmised from this that either ordinary gas ions result from an impurity always present (*e.g.* oxygen), a trace of which, far below the limits of analysis, would, owing to the extremely small amount of ions, meet the demand, or else that some equalising factor is at work, if the ions are actually formed from the substance of the gases.

There is more difference between positive and negative ions, as the latter travel faster; the difference is less when the gases are moist.

If the diffusion velocity of the ions, independently of electrical forces, is compared with that of the gas from which the ions have been formed, it is found to be smaller. The masses are therefore larger. The suggestion has been advanced that the ions consist of electrical nuclei, around which the uncharged molecules of the gas condense as dust.

While the mechanical nature of gas ions thus appears to be quite different from that which the kinetic theory requires of the molecules of a gas, their electrical behaviour has been found to be very simple. If the method (p. 509) of calculating the number of molecules from the mean cross-section (which can be deduced from diffusion experiments as well as from viscosity) is applied to gas ions, and if the total electric charge is determined at the same time, values are obtained for the number of ions in a mol, and for the charge on a single ion. The former agrees with that given on p. 510, and the latter with the value given on p. 538. Or, gas ions behave from the point of view of the kinetic theory like molecules of ordinary gases, and each ion carries the same charge as a univalent electrolytic ion.[1]

Electrons.—In addition to the positive and negative gas ions of fairly vague character, which have just been described, there is a special group of ions with much more definite properties than the others. They are negatively charged, and possess, in contrast with the relatively large and heavy gas ions, an extremely small mass. This does not approximate to the mass of molecules or atoms, but is about a thousand times smaller than the mass of a hydrogen atom. There is also considerable doubt whether it is a mass at all in a mechanical sense; there are reasons for the view that the energy which these particles possess in virtue of their velocity has its origin in electrodynamical effects, which are the consequence of its motion. These negative particles, which also have the above unit of electrical charge, are known as electrons. They are the last product of analysis in this region.

Electrons, like ordinary ions, can be produced in many different ways, but have always the same properties, apart from the differences in velocity, in whatever way they are produced. The simplest method of obtaining them is to pass electric discharges through gases at very low pressure. These then proceed, as has long been known, from the negative pole or kathode, the kathode rays, which travel in straight lines and transport a considerable amount of energy, which is transformed into other forms (heat, light, chemical action, Röntgen rays) when the rays meet objects placed in their path. A better name would be kathode streams, as they consist of negative particles projected rectilinearly, the individual existence of which has been proved experimentally, as will be shown immediately.

Kathode streams are deviated under the action of electric and magnetic fields; their velocity and the ratio between their charge and mass have been determined by measuring these effects.

The velocity is very great; for ordinary kathode streams it is about 3×10^9 cm. per second, which is only ten times smaller than the velocity of light. When the stream is sent out of the discharge tube through a window of thin aluminium (Lenard, 1898), the slower rays are sifted out, and those which remain have a velocity as high as 8×10^9 cm.

As experiments on the diffusion or viscosity of electrons cannot be carried out, other means had to be adopted to determine the

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[1] Isolated instances have been noticed in which ions occurred with double charges; still the simple ions were apparently in marked preponderance.

mass and charge of a single electron. Use was made of a special property of all gas ions: their power of acting as condensation nuclei in supersaturated vapours. By this means the electric charge associated with a single electron could be ascertained. Then the ratio e/m of the charge to the mass of an electron was found from the deviation experienced by the moving electrons or cathode currents under the influence of electric and magnetic fields. The latter experiments, performed in many different ways, gave results which closely agreed; the mean is about 10^7, when the quantity of electricity is expressed in electromagnetic c.g.s. units, and 10^8 when it is expressed in coulombs; the mass is measured in grams. The most accurate value is apparently $1{\cdot}86 \times 10^8$ coulombs per gram. From this, the mass m can be calculated if e is known.

Positive electrons have not yet been observed. Measurements similar to those described above were made with positive gas ions, and led to $e/m = 400$ in electrostatic units, *i.e.* a 25,000 times smaller number. As both carry the same charge, the difference is one of mass; the mass of a positive gas ion is about 25,000 times greater than that of a negative electron.

Ions as Nuclei.—It is evident from the considerations stated on p. 67 that a supersaturated vapour will not in general pass into the liquid state, and the less so the nearer it is to the equilibrium or saturation point. But if drops of water are present in the vapour, supersaturation is impossible. Other liquids or solids which are wetted by water or condense it upon their surface have the same action.

Taking into consideration also the fact that, as a result of surface tension, the vapour pressure of a small drop is greater the smaller its radius, we see that small drops are in equilibrium with a vapour which is supersaturated with respect to a plane surface to an extent which depends on the smallness of the drop. If, then, we have in a vapour drops of definite but unknown size, we can determine their radius if we determine the degree of supersaturation at which they begin to increase in size.

A measurable degree of supersaturation is obtained, for example, when air normally saturated with water vapour is suddenly, *i.e.* adiabatically, expanded, as a result of which it is cooled owing to the performance of external work. If the initial and final pressures are given, the lowering of the temperature and therefore the degree of supersaturation can be calculated (by means of the vapour pressure curve).

Now it has long been known that a jet of steam, in which there is a region of supersaturation before the region of condensation, forms a cloud, *i.e.* is very strongly condensed, on the approach of an electrically charged point (the same effect is produced in many other ways). (R. von Helmholtz, 1887.) Later researches, in particular a brilliant research by Wilson (1900), have proved this to be a specific effect of gas ions.

J. J. Thomson has suggested the following explanation of this action of ions. An electrically charged sphere strives to expand, for, since this would lower the potential while the amount of electricity remains the same, work would thereby be set free. If such a sphere of water is placed in saturated water vapour, it will condense water on its surface as a method of expansion, and equilibrium will result when the electrical work set free is equal to the work necessary for condensation from unsaturated vapour. The condensing effect is therefore greater the higher the potential of the charge on the drops. Thus the charge present on a gas ion will have a tendency to condense water on the ion; in order to reduce the potential it must therefore act as a nucleus for condensation.

This not only explains the above fact, but also suggests the possibility of individualising and counting the number of electrical charges and of ions. For, in contrast with most other effects, in which the sum of all the particles present is obtained, and which do not afford any means of distinguishing between separate particles and a continuous system, every particle here acts individually and summation occurs later, if at all.

The experimental idea is, therefore, to mix a measured amount of ions with air saturated with water vapour, and to count the number of fog particles which have been formed. This gives the number of nuclei. If some other property has been determined for the same amount of ions (*e.g.* the amount of electricity associated with it), this amount divided by the number of nuclei gives the value of that property for a single ion.

The formation of mist thus acts, as it were, as a physical microscope, for by means of it each individual ion, which is neither visible nor susceptible of examination, owing to its smallness, is so magnified that it is visible and can be examined. Or still better, it can be compared with the development of the latent photographic image, in which the supersaturated environment enlarges each invisible nucleus and renders it visible.

The mist particles are also very small, and it is only possible to count them directly in exceptional instances. But if the amount of condensed water is known from the degree of supersaturation, the determination of the size of one particle, or the average size of the particles, is sufficient for the calculation of the number. The size can be estimated from diffraction phenomena, the rate of falling and other properties.

By such methods, the experimental details of which cannot be described here, the following fundamental facts were established:

The electric charge of an electron is equal to the unit charge of an electrolytic ion, namely about 10^{-19} coulomb.

The ratio e/m of the charge on the electron to its mass was found to be 10^8 coulomb/gram (p. 537). As the charge is 10^{-19} coulomb, the mass m of an electron is about 10^{-27} g. As the mass of an atom of hydrogen is 10^{-24}, the mass of an electron is about one thousand times smaller than the mass of a hydrogen atom.

Besides electrons there are, as already stated, much larger gas ions, the mass of which considerably exceeds that of the molecule of the gas used; positive ions in particular only occur in this form. It is remarkable that these positive ions are considerably more difficult to condense with the aid of supersaturated water vapour than negative ions, and the difference between them is fairly constant. If the adiabatic expansion is below the ratio of 4 to 5, *i.e.* 1·25, no condensation takes place. Between 1·25 and 1·30 the negative ions alone condense, from this point onwards the positive ions also; thus with expansions over 1·38 double the number of mist particles are obtained as with expansions up to 1·25. No perfectly satisfactory explanation of this remarkable behaviour has as yet been found.

The Electron Theory.—Although the experimental proof of the individual existence of electrons is based exclusively upon the above experiments on their condensation of supersaturated water vapour, it has been considered a satisfactory foundation on which to make very extensive theories. It was an important point that the charge on an electron was found to be the same as that on an electrolytic ion, *i.e.* 10^{-19} coulomb. Helmholtz had long ago (1879) regarded this as the smallest possible unit of electricity, and attributed an atomic structure to electricity.

The simplest application of this theory is to electrolytic ions, which, from this point of view, are compounds of chemical atoms with as many electrons as its valency amounts to. These compounds are separated by electrolysis, the chemical atom remaining behind in the electrolyte or on the electrode, while the electrons travel further into the metal. Metallic conduction must be regarded as a migration of electrons in the metal.

It must be remembered that positive electrons are not known, but only positive atoms, or gas ions and kations. We may either assume that positive electrons similar to negative electrons exist, but have not been isolated, or we may consider the positive state to be produced by the loss of a negative electron in the system. In view of the want of perfect symmetry between positive and negative electricity, as shown in certain electrical phenomena, the second assumption (which corresponds to Franklin's old theory of electricity, only the signs are reversed) is preferable. Negative and positive electricity would thus be comparable with regions in the atmosphere, where the pressure is higher or lower than the mean. Both can perform work in accordance with analogous laws, but neutralise each other (become zero) when brought together, and can, in obedience to the law of conservation of electricity, be produced anew at any desired place, but only simultaneously and in equivalent amounts.

It is more difficult to apply the theory to chemical compounds. A valency cannot be put simply equal to an electron, for substances with free valencies, like nitric oxide and carbon monoxide, do not show free electrical charges at all; nor are any other special electrical properties recognisable in any other direction.

It is a very remarkable indication that the mass of the electron depends on its velocity, and appears to approach zero, when its velocity approximates to the velocity of light. The idea is not far to seek that the nature of mechanical mass is electrodynamical, just as the variable mass of the electron is, and serious endeavours are being made to replace the mechanical conception of the physical world by an electrodynamical one. Although these efforts have not yet led to complete results, they prove that what many philosophers considered a necessity of thought, namely to reduce all phenomena to a mechanical basis, has been no necessity, but only a practice of doubtful value.

A further fact which indicates the close connexion with mechanical properties was discovered by Lenard (1898); the absorption of very rapid electron streams by the most diverse substances is a function of their density alone, and not of their chemical nature. Hitherto it has been exclusively in mechanical phenomena that mass has functioned as a sufficient and controlling factor, and we are thus justified in representing the absorption of electrons as a purely mechanical phenomenon.

Endeavours to represent the ponderable atoms as systems of electrons point in the same direction. The old chemical hypothesis that all the elements are compounds of a primal matter has been revived very recently in consequence of the transformations of the radioactive elements (see below); the objection based on the irrational ratios of the atomic weights has lost its force, since the mass of the electron is so small that the lightest of all atoms, that of hydrogen, must, according to this theory, consist of about 1000 electrons. For, since the combining weight of no element is known with certainty to the third decimal place, the number of electrons cannot be established within the limits of error, in whole numbers even, so that there can be no question of testing whether fractions occur (cp. Bernoulli, 1908).

Radioactive Substances.—On the grounds of a conjecture, which turned out to be wrong, H. Becquerel (1896) found that uranium salts produce a developable impression on a photographic plate, even when they are separated from it by black paper or a sheet of other light-tight material. The effect of the various compounds was practically proportional to the uranium content, but uranium minerals were afterwards found which showed a much stronger action. Starting from the assumption that this was due to admixture with some other substance which had a stronger action than uranium itself, P. and S. Curie carried out separations on this mineral (uranium pitchblende). Just as Bunsen had employed spectrum analysis as a guide in concentrating and preparing rubidium and cæsium in a pure state, so M. and Mme. Curie made similar use of this action, or rather of an allied action. Röntgen rays, the analogy with which served as the starting-point of the series of investigations, not only act on the photographic plate, but also cause air to conduct and phosphorescent substances to become luminous, and uranium rays have the same effects. The second of these actions is easily followed by means of the discharge of an electroscope, and so the rate of discharge of an electroscope under the influence of the various fractions was determined, and served as a guide in the search for the unknown substance.

The result was that on the one hand a substance similar to bismuth with a strong radiation began to separate, and on the other one similar to barium. The former was provisionally named Polonium, but has not yet been prepared pure. The other was named Radium, and is now known in as pure a state as any other element.

The combining weight of radium is Ra = 226·4, and it takes its normal place in the periodic system as the last bivalent element in the column of the alkaline earth series. All its reactions correspond to this position, for they are as like the reactions of barium as cæsium reactions are like those of potassium. The flame colouration is not green, but red, and the solubility of most of its salts is smaller than that of the corresponding barium salt. No analytical reaction which effects a fairly clean separation of radium and barium has been found, presumably because the purely chemical behaviour of radium has not been sufficiently investigated; the only method available is the fractional crystallisation of the chlorides or bromides, which apparently form an isomorphous solution, rendering the separation tedious in the extreme. The amount of radium in pitchblende is so very small, that the total amount of pure radium compounds in the hands of investigators probably does not exceed ten grams.

Radium compounds exhibit in the highest degree the above characteristic of activity proceeding from it, as it continuously produces energy. This is manifested not only in the manner described, but also in the form of heat, for the contents of a vessel containing radium are maintained at a higher temperature than its environment, as can easily be shown directly by means of a thermometer. Exact measurements have shown that one gram of radium evolves $1{\cdot}2 \times 10^{-6}$ erg per second. The amount varies a little with the previous treatment of the preparation, but is always reproduced when it is left to itself. The chemical combination in which the radium happens to be has also no effect on the amount. Temperature was at first held to be also without effect on it, but recently an acceleration has been observed at higher temperatures, which is lost again on cooling. This effect is very small (Engler, 1908, and others).

The apparent contradiction between this continuous production of heat and the first law of energetics was removed by the recognition of it as a heat of reaction, which had its origin in a continuous and spontaneous transformation of the radium. Various products are formed; as will be explained immediately, helium has been shown with certainty to be the end product (Ramsay and Soddy, 1903). The preservation of the one law has therefore only been possible at the expense of another, the law of the conservation of the elements (p. 111). Or it will be necessary to doubt the elementary nature of all the elements, and to subject them to a fresh scrutiny, for which purpose the new source of enormously concentrated energy, which radium presents, may possibly provide the means.[1]

It was natural that the discovery of these remarkable properties of uranium and its minerals should be followed by extensive searches for other radioactive substances. The only one of the known elements which was found to be active was Thorium (Schmidt, 1898; Curie, 1898), although it was established that activity is a very widespread phenomenon. In particular, water and air from somewhat considerable depths of the earth are always more or less active, although the activity varies very much according to the locality.

Since uranium and thorium are the elements with the highest atomic weight, there seems to be some connexion between activity and it, the more so as radium comes next. The large number of gaps in this part of the table may then be connected with the instability of all elements with high atomic weight (see below).

The Transformation Theory.—Since the action of uranium and radium rays presented so many similarities with Röntgen rays, investigations were at first confined to their similarity to light, and without much result. Then Rutherford and Soddy were bold enough to conceive these actions as chemically materialistic, and this proved to be the key to the comprehension of the whole phenomenon. It was found that the active principle of thorium was carried along by a current of air, could be condensed by means of liquid air, and, in short, behaved like a gas. This gas had the same power as radium of acting upon the photographic plate, of exciting

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[1] The transformation of copper into lithium under the influence of radium emanation, reported by Ramsay, has been called in question by S. Curie. As, however, the formation of helium from radium has been frequently confirmed, the fundamental proof of the transmutability of the elements is forthcoming, and the results of the scientific investigation of these new reactions can be awaited in patience.

phosphorescence, and of ionising gases. Only it retained these powers for a very short time, and, with them, its existence; it disappeared, and a solid which was soluble in acids appeared in its place. It could not be seen, to be sure, the indications of its presence being that the surfaces of all objects which had been in contact with the gas showed radioactive properties, which could be removed from them by washing with acid. This solid deposit disappeared spontaneously after a time.

All these complicated phenomena can be explained on the assumption that thorium is constantly being transformed into another substance, the active gas known as emanation, which also undergoes similar transformations. The only one of these substances which has been seen is the gaseous emanation of radium, which has a much longer life than thorium emanation, and is also formed in much larger amount. Its spectrum has been observed, and by this means the final transformation into helium, which also has a very striking spectrum, has been established. The chemical characteristics of the others are at present restricted to their solubility or insolubility in certain reagents; they have never been obtained in sufficient quantity to permit of their being seen and studied in the same manner as other substances. Their general characteristic is the power of ionising gases and making them conduct. There are qualitative differences in the nature of the rays in this respect (see below); the action is at first proportional to the amount; but there are so many contingent circumstances, since the formation of gas ions is not the primary effect, that the main phenomenon is often masked and destroyed. The specific velocity of reaction with which the various substances are transformed has been found to be very characteristic.

The Velocity of Transformation.—This transformation is quite decisively a reaction of the first order, *i.e.* the velocity is proportional to the quantity of reacting substance. No other factor, such as temperature or concentration, comes in; even the state of chemical combination has no effect. If, then, a is the amount of active substance present, the amount da decomposed in the time dt is simply proportional to a and to a velocity constant which (apart from the very slight temperature effect mentioned on p. 542) is not affected by any constant condition; the equation is thus $-da/dt = ka$. As shown on p. 290, for finite quantities the equation becomes $a_0/a = e^{kt}$, where a_0 is the initial amount, a the amount at the time t, and e is the base of the natural logarithms, the number 2·7183. As both a_0 and a appear as a ratio, their absolute amount does not matter, nor does the unit in which they are measured, as it disappears in the fraction. It is thus not necessary to know the absolute amounts, provided the relative amounts are known. The latter are derived from the ionising power under comparable conditions. By ascertaining this for two different times, we obtain the ratio a_0/a and the time t, from which k can be calculated.

This is done by taking the natural logarithms of both sides, from which $\lg a_0/a = kt$, or $k = \frac{\lg (a_0/a)}{t}$. Using ordinary logarithms we have $k = \frac{\log (a_0/a)}{\cdot 4343t}$ or $= \frac{\log a_0 - \log a}{\cdot 4343t}$.

The formula has the following meaning. If any two observed values of a_0, a, and t are put in the equation, the same value of k is always obtained for the same radioactive substance, independently of the amount, the state of combination, or any other circumstance. The constant k is therefore a perfectly general analytical characteristic of the substance, in precisely the same way as a line in the spectrum, or a colour reaction, but much more general because much more independent. It is comparable in this respect to the combining weight, only it is much more easily determined.

The process usually adopted is slightly different; instead of measuring a_0 and a for any arbitrary time t, the time is so chosen that the ratio a_0/a is 2, or, in other words, what is determined is the time necessary for half decomposition. In this case $a_0/a = 2$, and the equation becomes $k = \lg 2/t$ or $kt = \lg 2$. Since the right side of the equation is constant, kt is also a constant, and the time for half decomposition is inversely proportional to the constant k; it is as characteristic of the radioactive substance as k is, and it is preferred for this purpose on account of its plain meaning. It is known as the half life or period of half decay. If l is this value, the relation is obtained $kl = \lg 2 = \cdot 6931$, or $l = \cdot 6931/k$; by means of this equation the constant can be calculated from the half period, and conversely.

The Kinds of Radiation.—Another means of distinguishing between the various radioactive substances is found in the nature of the energy emitted. There are three different kinds, known as α, β and γ radiation. The difference between them is very well illustrated by the diagram, Fig. 67, given by S. Curie, which shows the radiation of radium (which contains all three). R is radium which is contained at the bottom of a narrow lead cylinder, and can therefore send rays upwards only; above R is a magnetic field, the north pole of which is in front of the paper and the south pole behind the paper. The α-rays are feebly diverted to the left, the β-rays strongly to the right, while the γ-rays are unaffected. The α-rays have a comparatively small velocity, are shown by the direction of their deviation in the magnetic field to be positively charged, and have the properties of positive gas ions. The β-rays behave in essentially the same way as kathode rays, *i.e.* they are to be regarded as a stream of negative electrons. The γ-rays have the greatest resemblance to Röntgen rays.

Apart from their behaviour in a magnetic field, the three groups can be distinguished by their penetrating power. The α-rays are the weakest in this respect, since they are reduced to one half by aluminium foil of ·0005 cm. thickness; they can penetrate only a few cm. of air, by which they are soon absorbed. The β-rays are about 100 times more penetrating, and the γ-rays about 10,000 times more penetrating than the α-rays; the γ-rays can penetrate 8 cm. of aluminium, without losing more than half their strength.

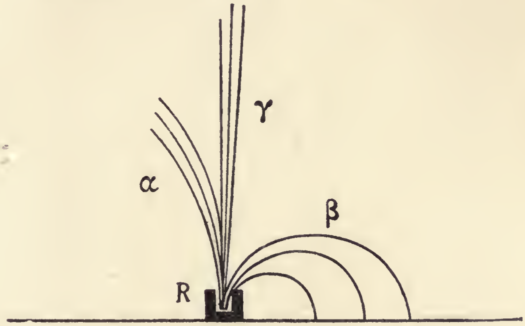

FIG. 67.

Transformation Products of the Radioactive Elements.—Owing to the novelty and diversity of the phenomena displayed during the gradual transformation of radioactive substances, there is a considerable amount of confusion in the literature regarding their relations. Although Rutherford and Soddy's theory of the gradated decay of the products has contributed greatly to the orderly arrangement of the facts, the facts are still in course of evolution, and a fairly comprehensive review is not yet possible. To give an idea of the main phenomena, the following table, given by Rutherford (1905) and summarising his results, is appended :—

Product.	k.	Average half-period.	Kind of Rays.	Chemical and Physical Properties.
Uranium ↓	...	...	α	soluble in excess of ammonium carbonate, soluble in ether.
Uranium X ↓	$3{\cdot}6 \times 10^{-7}$	22 days	β and γ	insoluble in excess of ammonium carbonate, soluble in ether and water.
Thorium ↓	...	...	α	insoluble in ammonia.
Thorium X ↓	$2{\cdot}0 \times 10^{-6}$	4 days	α	soluble in ammonia and water.
Emanation ↓	$1{\cdot}3 \times 10^{-2}$	53 seconds	α	gas of the argon type, high molar weight, liquid at −120°.

Product.	k.	Average half-period.	Kind of Rays.	Chemical and Physical Properties.
Thorium A ↓	$1{\cdot}74 \times 10^{-5}$	11 hours	o	is precipitated on solids, collects on the kathode in an electric field. A is more volatile than B. Distinguished electro-chemically.
Thorium B ↓	$2{\cdot}2 \times 10^{-4}$	55 minutes	α, β, γ	
Actinium ↓	...	...	o	insoluble in ammonia.
Actinium X ↓	$7{\cdot}8 \times 10^{-7}$	102 days	$\alpha, \beta(?)$	soluble in ammonia.
Emanation ↓	$\cdot 17$	3·9 seconds	α	gas.
Actinium A ↓	$3{\cdot}2 \times 10^{-4}$	36 minutes	o	precipitated on solids, collects on the kathode in an electric field. Soluble in ammonia and strong acids. Volatile at 100°. Can be separated by electrolysis.
Actinium B ↓	$5{\cdot}4 \times 10^{-3}$	2·15 minutes	α, β, γ	
Radium ↓	...	1300 years	α	like barium.
Emanation ↓	$2{\cdot}1 \times 10^{-6}$	3·8 days	α	dense gas of the argon type, liquid at −150°.
Radium A ↓	$3{\cdot}85 \times 10^{-3}$	3 minutes	α	precipitated on solids, collects on the kathode in an electric field, soluble in strong acids. B is volatile at 700°, A and C at 1000°.
Radium B ↓	$5{\cdot}38 \times 10^{-4}$	21 minutes	o	
Radium C ↓	$4{\cdot}13 \times 10^{-4}$	28 minutes	α, β, γ	
Radium D ↓	...	*ca.* 40 years	o	soluble in acids, volatile below 1000°.
Radium E ↓	$1{\cdot}3 \times 10^{-6}$	6 days	β, γ	not volatile at 1000°.
Radium F	$5{\cdot}6 \times 10^{-8}$	143 days	α	precipitated from solution by bismuth, volatile at 1000°, has the properties of radiotellurium and polonium.

The following remark must be appended to this table. Since the radioactive elements are engaged in a continual self-destruction, they should generally have more or less completely vanished, although from the velocity equation the last traces would cease to exist only after an infinite time. The explanation of their occurrence in quite notable quantity is that they are at the same time regenerated from the other radioactive elements. If A changes into B with a certain velocity, and B into C, etc., the ratio in which they are found together after a long time will be the inverse of their transformation velocities. This is on the assumption that the weight is unchanged by the transformation. If this is not the case, the ratio of the initial and final weights must be introduced as coefficients of the relative amounts.

Now it has actually been found that, *e.g.* in the uranium minerals, the radium is in a fairly constant ratio to the uranium, and the idea is not far to seek that radium is a transformation product of uranium, and that the ratio by weight represents the ratio of their lives. It would then be possible (and scientifically necessary) to outline a genealogy of the active elements, representing their transformations. This is done in the table on pp. 545-546.

Uranium is regarded as the primogenitor of the elements; its transformation velocity is so small that it has not yet been measured directly. From the above considerations its life has been estimated to be 6×10^8 years. Its first transformation product is a much more active substance, which can be so far separated by chemical methods that fractions of much greater activity can be obtained. The weaker uranium residue regains its normal strength in a few weeks. The radiation of an old preparation does not come from the chief constituent alone, but from all its transformation products, which have accumulated in it according to their lives. The half-period of uranium X is 22 days.

The direct transformation of uranium X into thorium has not been observed, and the sequence expressed in the table is hypothetical. The position of thorium, too, has not yet been cleared up, as its elementary nature has been called in question without any decisive conclusion being arrived at. In any case a very active solid is formed in thorium preparations, just as in uranium compounds, which has the general character of a metal; the half-period is four days, and it is transformed into an emanation, the half-period of which is only about one minute. In other respects it is a gas of the same type as argon, *i.e.* it does not enter into chemical combination. Diffusion-experiments give a high molar weight (at least 100), and the isolation was effected by means of liquid air, which condensed the gas at − 150°.

All solids, which come in contact with emanation, are covered with an active layer, which was known as "induced activity" before the materialistic theory of activity was accepted; it is soluble in acids, and behaves like a heavy metal, or its oxide. This thorium A is inactive, and its existence was deduced from the fact that it changes into an active product of very short life, which resembles thorium A in other respects, but can be separated from it.

The next stage, which is also hypothetical in its relation to thorium, is actinium, an element with the general character of the rare earths, which was discovered some time ago (1899) by Debierne, but has not yet been obtained sufficiently pure to permit of accurate description. There seems to be no doubt about its individuality.

The transformations of actinium are very similar to those of thorium. The first step is an element of similar nature with a short half-period, succeeded by a very short-lived emanation of the type of argon, and then by a closely related pair of heavy metals, the first of which is inactive.

The next permanent stage is radium with its accurately ascertained half-period of 1300 years. When freed from its transformation products, it sends out only α-rays. It passes directly into an emanation of the usual type, which, in virtue of its much longer half-period of 3·8 days (that of actinium is only about 4 seconds) was earlier and much better known than any of the other emanations. Very large amounts of energy are set free by its decomposition; water is decomposed into hydrogen and oxygen, glass is coloured violet or brown, and apparently much more extensive chemical changes are effected by it. By its transformation various solids are formed, as given in the table. The last product, which is possibly the first member of a new series, as its half period is 143 days, is very probably identical with the first strongly active element isolated from pitchblende, the polonium of S. Curie (p. 541).

It must be repeated that this table will undergo many alterations. The regularities which are already recognisable are indeed remarkable. Not only do the series of transformations always proceed by way of a gas of the argon type, and the half periods of the successive products follow in the same order, but there is also a striking relation to the periodic system. Uranium belongs to the hexavalent group; it is followed in the table by members of the quadrivalent, trivalent and bivalent groups. This suggests the possibility that there is a quinquivalent element[1] between uranium and thorium, and that polonium belongs to the silver and gold group, and would thus come into the univalent group. At any rate, the existence of an alkali metal of high combining weight has lately been made very probable.

The above sketch of this new subject merely purports to give a general idea of the new and important facts which the last decade has brought forth. With the rapid development of science at the present time, it will in a few years be possible to give a general synopsis of the subject without too many hypothetical constituents. One result of the present-day rapid development of science is that work is published more hastily, and many unstable intermediate steps, which, under the old system of slower production, disappeared after they had served their turn, now enjoy their brief existence in the literature under all eyes. The unfortunate thing is that no formal notice is given of their decease.

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[1] This may possibly be the recently discovered Ionium.

BOOK VII

CHEMICAL AFFINITY

CHAPTER XXVII

METHODS

The Problem.—The problem before us now is what will occur when a number of substances are mixed in definite proportions under given conditions. In general they will not be in chemical equilibrium, and consequently decompositions, combinations, and separations will result until equilibrium is reached.

The formal side of this question has been dealt with, so far as the present state of chemical science will permit, in the second part of this work; and the two fundamental laws of equilibrium, the law of mass-action and the law of reaction against changes produced by external forces, have been discussed as the most general form of answer to this question. These processes, both in their course and in the final equilibrium, have been found to be characterised by coefficients, which are dependent on the chemical nature of the substances and on the external conditions of the process. But the only question considered in connexion with these coefficients was how far they could be regarded as constants. We shall now consider the further question as to the connexion between these coefficients and the chemical nature of the substances and the external conditions. Thus the abstract considerations of chemical energetics become endowed with life, and the stoichiometric problems, which were the subject of the first part of this work, come into view again as the final aim of the later developments of general chemistry.

Since these coefficients define the equilibrium between the substances, the problems how far a system is from equilibrium, and what work it can perform before it reaches this condition, are capable of solution. But this is the main question in all applications of chemical processes, *e.g.* in technical and physiological chemistry, and it is a matter of the first importance in reviewing the results of processes to have an answer to it.

In addition to the total work, which is connected with a given change of state, there is the question of the velocity with which the final state is reached. This also is of the greatest importance in all applications of chemical processes, for just as it is not a matter of indifference to the technical chemist whether he can prepare his products in a day or a week, so in a living organism every activity is decisively influenced by the rapidity or slowness of the corresponding chemical reactions.

Two groups of constants are therefore required for an answer to such questions: equilibrium constants and velocity constants. There is this relation between them, that the equilibrium constant can always be represented as the ratio of two velocity constants belonging to the opposed reactions. The former can be deduced from the latter if they are known; but very different velocity constants are possible for the same equilibrium, so long as the two velocities vary to the same extent. In fact, the velocities can in certain cases be altered to a great extent by catalysers, without affecting the equilibrium at all.

Measurements.—In each case the determination of the constant is effected by estimating at a given moment the amounts of the different substances present in the system. In the simple case of a single substance in one phase this is the common problem of analysis. The determination of the dissociation pressure of calcium carbonate, or the solubility of an indifferent substance, is an example.

It is a more difficult matter if several substances are to be estimated in the same phase. Ordinary methods of analysis often fail to solve the problem. As a rule, in chemical analysis the substance to be determined is converted into another form, which admits of separation and measurement; the process only succeeds when the quantity of the substance to be estimated is not changed by this operation. Now, such a change always occurs, if the substance is a component of an equilibrium which depends on the concentration of it, provided that the velocity of the reaction is of the same order as the process made use of in the analysis. The error introduced by this is negligible only in those cases in which the velocity with which the equilibrium is established is sufficiently small.

If, for example, the quantity of silver ion in a solution of silver acetate is to be determined, the analytical process of precipitating silver ion by means of chloride ion cannot be employed. For, although the addition of chloride ion as hydrochloric acid precipitates at first only the silver ion present, silver ion is reproduced from the undissociated silver acetate, and this is at once precipitated, until at the end the precipitate contains not only the silver ion actually present from the beginning, but all the silver ion which could be formed under the conditions, *i.e.* the potential silver ion.

On the other hand, the quantity of chloride ion formed under given conditions by the hydrolysis of monochloracetic acid, can be determined quite well in this manner, for, as experiments show, no silver chloride is precipitated from pure monochloracetic acid and silver solutions at room temperature in the time necessary for an analysis. It is not that this reaction ceases during this period; the velocity is so small that the quantity of silver chloride formed in the time can be made vanishingly small in comparison with that formed from the chloride ion present.

The Fixation Methods.—When the alteration of the quantity of the substance to be determined is too great to be neglected, the analysis can often be carried out by bringing the system into a condition in which the velocity is very small, without changing the quantity of the substance to be determined. Since lowering the temperature is the most general method of diminishing the velocity of reaction, it is successfully employed in very many cases. But it must be effected so rapidly that the equilibrium has not time to change during the cooling, where the system is still in the region of finite reaction-velocity; and, if necessary, special arrangements (leading through cooled tubes, etc.) must be made in order to fulfil this condition.

Such a process has been employed in the study of the reaction between hydrogen and iodine (p. 337). After being heated for longer or shorter periods of time at the appropriate temperature, the vessel was cooled as rapidly as possible in order to fix the system. It is possible to find out whether this has been attained by repeating the experiment under the same conditions, but increasing the time of cooling to a known extent, and observing the difference caused by it. The possible error may also be approximately estimated by means of the temperature coefficients of the reaction velocities.

In addition to the lowering of temperature, there are chemical methods of fixation, which can be made use of in special cases. Reactions which are accelerated by the presence of certain substances, can be stopped by removal of these substances, or by converting them into other substances. Addition of "negative catalysers," *i.e.* substances which diminish the velocity of reaction, produces the same effect. Although the former of these methods has been frequently used, there is no instance of the latter being used in actual practise.

Chemical fixation is often used in the catalysis of cane-sugar by means of acids (p. 291), the acid being neutralised at the given moment by addition of a base. As the quantity of the base cannot be easily measured, and excess has an effect upon the rotation, it is simpler to add sodium acetate. The concentration of hydrion is greatly diminished as a result of the equilibrium between the ions (p. 414), and in consequence the velocity becomes so small as to be negligible.

Blank experiments must be made in this case also, in order to be certain that the method has no effect on the magnitude to be measured.

Should these means fail, we are confronted with the general problem of determining the amount of a given constituent of a mixture without interfering with it in any way. The simplest method of dealing with it is to choose the conditions of experiment in such a way that the amounts of all but one substance are known; if the total quantity is determined, the desired value is given as the difference.

Deville used this method in his determinations of the equilibrium between iron and water vapour. The pressure of water vapour was kept at a constant known value by surrounding the water vessel with a constant temperature bath; subtraction of this pressure from the total pressure gave the pressure of the hydrogen gas produced in the reaction.

Physical Methods.—If several substances change their concentrations independently at the same time, this solution is not available. The physical methods, as they are called, must be employed.

All analytical methods which find employment in chemistry are, strictly speaking, physical, since they depend on the measurement of weight, volume, or some other physical property. The essence of the chemical methods is that when the usual physical methods of weight or volume determination do not suffice to effect the measurement, chemical processes are introduced, which admit of the physical separation of the substance (or of some transformation product), and the subsequent application of these methods. Physical methods, by a suitable choice of the property made use of, dispense with the necessity for separation or previous chemical action.

The physical methods depend on the measurement in a mixture of some property which varies simultaneously with the amount of the substance to be estimated. The relationship between the property and the amount of substance must be known.

Two kinds of properties are available. They may be special properties, which belong alone to the substance in question; in this case, measurement of the property gives at once the quantity of the substance. Or they may be general properties, common to several or all of the substances present. The latter will be considered first, as it is the more general case.

The choice of a property for this purpose is limited by the condition that it must be constitutive as regards the process under investigation, *i.e.* the total change of this property during the process must have a finite value. Additive properties, on the other hand, undergo no change in total amount, even though the individual substances have changed; such properties are of no use for this purpose.

No strictly additive properties are known other than mass and weight, so that any other property might be used. But the deviations from the additive character are often so slight that the influence of the experimental error is too great for the results to be of any use. The choice of the property is determined by the ease and accuracy with which it may be ascertained; the amount of change which takes place during the reaction is also an important consideration. It is also important that the change of property and of amount of substance shall be proportional to each other. This always holds for small quantities: the limit, where this is no longer true, must be ascertained in each case.

General Theory.—This proportionality is assumed in the following discussion.

Suppose the reaction to be represented by the chemical equation $A_1 + A_2 + A_3 + \dots = B_1 + B_2 + B_3 + \dots$, and the values of the selected property for one mol (or as many mols as there are in the equation) of A_1, A_2, A_3 . . ., and of B_1, B_2, B_3 . . ., be α_1, α_2, α_3 . . ., and β_1, β_2, β_3 . . ., respectively. Then $\alpha_1 + \alpha_2 + \alpha_3 + \dots = \Sigma\alpha$, is the fraction of the total which is due to the substances on the left side of the equation, while $\Sigma\beta$ is the corresponding fraction for the right side. The alteration on complete transformation of A into B is therefore $\Sigma\alpha - \Sigma\beta = R_0$, and if only the fraction x is transformed, the change amounts to $x(\Sigma\alpha - \Sigma\beta)$ or xR_0.

Now let A and B be present in the amounts a_1, a_2, a_3, and b_1, b_2, b_3, a and b being expressed in terms of A and B as units; the mixture would possess this property to the amount $a_1\alpha_1 + a_2\alpha_2 + a_3\alpha_3 + \dots + b_1\beta_1 + b_2\beta_2 + b_3\beta_3 + \dots = \Sigma a\alpha + \Sigma b\beta$. After the unknown quantity x has been transformed, the value R of the property is measured, and from it x is to be calculated.

R is given by the expression $R = (a_1 + x)\alpha_1 + (a_2 + x)\alpha_2 + (a_3 + x)\alpha_3 \dots + (b_1 - x)\beta_1 + (b_2 - x)\beta_2 + (b_3 - x)\beta_3 \dots$, since a_1, a_2, a_3 . . . have increased by the same amount x, while b_1, b_2, b_3 . . . have diminished to the like extent.[1] The expression can be written in the form $R = \Sigma a\alpha + x\Sigma\alpha + \Sigma b\beta - x\Sigma\beta$ or $R = \Sigma a\alpha + \Sigma b\beta + xR_0$, whence

$$x = \frac{R - (\Sigma a\alpha + \Sigma b\beta)}{R_0}.$$

Remembering that $\Sigma a\alpha + \Sigma b\beta$ is the value of the property in the

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[1] The value of x may be negative.

original mixture, and R the value after the amount x has been transformed, we see that in the numerator of the fraction we have the change of the property during the chemical change; this we may write ΔR. The denominator R_0 is the change for the complete transformation of a formula-weight of the substance. This ratio gives the amount of transformation, which is accordingly calculated from the equation

$$x = \frac{\Delta R}{R_0}.$$

Applications.—Gladstone was the first to apply physical methods in a systematic manner to the solution of the problems of affinity. From his researches we can at once see the multiplicity of forms that can be assumed by the physical methods according to circumstances. Besides change of colour, which he preferred, he turned to account fluorescence, circular polarisation, and the phenomena of diffusion. The quantitative development of the method, however, was only partially carried out by him.

An example of the physical method in a fully developed form is first found in Julius Thomsen's calorimetric researches (1869), which yielded all the necessary information as to the distribution of substances in a homogeneous liquid.

The coefficients α and β are here simply quantities of energy. If we deal, for example, with the action between sodium fluoride and hydrogen chloride, hydrogen fluoride and sodium chloride being formed, we have

α_1 the energy of 1 mol of sodium fluoride,
α_2 ,, ,, ,, hydrogen chloride,
β_1 ,, ,, ,, sodium chloride,
β_2 ,, ,, ,, hydrogen fluoride.

In the equation

$$x = \frac{\Delta R}{R_0}$$

ΔR denotes the change of energy in passing from the initial to the equilibrium state; it is consequently the thermal effect of the action of hydrochloric acid on sodium fluoride. The denominator is the difference of energy between sodium fluoride plus hydrochloric acid, and sodium chloride plus hydrofluoric acid, *i.e.* the difference of the heats of neutralisation of the two acids.

Now the heat of neutralisation of hydrofluoric acid is 68·05 kj., and of hydrochloric acid 57·48 kj.; the difference is 10·57 kj., so we have $R_0 = -10{\cdot}57$ kj. On the other hand, when 1 eq. of hydrochloric acid acts on 1 eq. of sodium fluoride there is observed a heat-absorption of 9·87 kj. Substituting these values, we obtain

$$x = \frac{-9{\cdot}87}{-10{\cdot}57} = 0{\cdot}933.$$

In this process, therefore, 0·933 of the equivalent or 93·3 per cent of the hydrofluoric acid is liberated by the hydrochloric acid.

Corrections.—We have, in arriving at this result, made the tacit assumption that no other alteration of energy takes place beyond that occasioned by the double decomposition. Now this supposition is not always correct; the substances present often act in quite another direction also, so that corresponding corrections must be applied. This is done by determining the thermal value of the secondary reactions by means of special experiments, and deducting it from ΔR. The formula then is

$$x = \frac{\Delta R - q}{R_0}.$$

In many cases there is encountered the difficulty that q itself is a function of the value x to be determined. It is then simplest to calculate the values of R and q for some arbitrary values of x, which are to be so chosen that the real value of x falls between them, and can be calculated with sufficient accuracy by interpolation.

Indirect Methods.—In many cases $\Sigma\alpha$ and $\Sigma\beta$, from which R_0 is obtained, cannot conveniently be measured directly. For instance, the heats of neutralisation of soluble bases can readily be obtained, but not so in the case of insoluble bases. There is, however, an important general method by which these values may be determined in another way.

Starting from either of the states represented by the two sides of the chemical equation, the same intermediate state is reached; the difference of these two changes is equal to the desired difference for the complete transformation from the one end state to the other one. If we proceed from the first state to equilibrium, in which the value is S, the difference observed is $\Sigma\alpha - S$. From the other end, the value for the equilibrium still being S, the observed difference is $\Sigma\beta - S$. The difference of the two changes is $(\Sigma\alpha - S) - (\Sigma\beta - S) = \Sigma\alpha - \Sigma\beta$, the desired value.

The process assumes that the substances are employed in the ratio given by the equation, on each occasion the amounts of substances represented by one or other side of the equation being caused to interact. It is also assumed that real equilibrium is attained from both ends; in very slow reactions special precautions must be taken to ensure that this is so.

To find the heat of neutralisation, for example, the salt of the first acid is acted on with the second acid, and the experiment repeated with the salt of the second acid and the first acid in the free state. These give the necessary data for calculation of the partition, for $\Sigma a - S = \Delta R$.

The Volumetric Method.—A process equal to the calorimetric method in applicability, but much easier and more convenient to perform, is the volumetric method based on the determination of the specific volume. The utilisation of specific gravity for the quantitative estimation of dissolved substances reaches back to antiquity, and to-day occupies an important place in the arts and in science. It is therefore surprising that the application of this method to the determination of the distribution of substances in homogeneous solutions was so long delayed. The first experiments were made by Tissier in 1859. Ostwald afterwards (1878) made numerous measurements by this method on the distribution of different bases between pairs of acids acting simultaneously.

If d is the specific gravity of a liquid, then l/d is its specific volume, *i.e.* the volume occupied by unit weight. Multiplying this by the weight of the solution containing one mol of the substance considered, we obtain the molar volume of the solution. If we bring together different solutions that can act chemically on each other, and so let the process take place, the molar volume of the mixed solution is seen to be different from the sum of the volumes of the components.

The alteration of the molar volume on neutralisation is moderately large, and is much more varied than is the case with the corresponding heats of neutralisation. The underlying principle is the same, and the formula

$$x = \frac{\Delta R}{R_0}$$

still holds good, the letters having merely a correspondingly altered significance. ΔR is the change of volume occasioned by the action of the one acid on the neutral salt of the other, and R_0 is the difference of the volume changes on neutralisation of each of the acids. If secondary actions take place, we get the corrected formula

$$x = \frac{\Delta R - q}{R_0},$$

q being the change of volume consequent on the secondary reactions.

The actual carrying out of the experiments can easily be brought to a high degree of accuracy by the use of the Sprengel pycnometer. The procedure is the same as in ordinary determinations of density; the temperature must be carefully kept constant, and if the pycnometer be capable of containing 20-30 g., the error is only a few units in the fifth decimal place.

To take an example: the specific volume of a potassium hydroxide solution, containing KOH = 56·1 g. in a kilogram, was found equal to ·950668; that of a corresponding solution of nitric acid equal to ·966623; the molar volumes are 950·668 and 966·623 ccm. After mixture of equal weights of the two solutions, the specific volume of the potassium nitrate solution obtained was ·968669; the molar volume (there being now 2000 g. of solution) is therefore 1937·338 ccm., while the sum of the molar volumes of acid and base is only 1917·291 ccm. Consequently, on neutralisation, there is an expansion of 20·047 ccm.

The alteration is usually smaller than this; for the fatty acids it falls as low as 6 ccm.

The volumetric method can easily be extended to higher and lower temperatures. We have only to determine the thermal expansion of the liquids whose volumes are to be compared, in order to obtain the material necessary for calculating the distribution of the base between the acids for every other temperature.

Another general property which can be used in the same manner, and has been so applied, is refraction. Since no new principle is involved, details need not be given. This does not exhaust the list of general properties which might be employed, but none of the others have been made use of to any extent.

Special Properties.—The most favourable cases for the application of special properties occur when a property can be found which is not shared by the other substances present, and whose amount is proportional to its concentration. Measurement of its magnitude gives directly the desired quantity.

There is a possibility of error, if the assumed proportionality is not exact, or if the factor is affected by the presence of other substances which do not possess the property in question. It is not always easy to make control experiments, for a change of value of the property may either be due to the change in the amount of the substance, or to a change in the factor. The only means that can be employed in such cases is to measure another independent property. Comparison of the two results will show which of the two possibilities is the more probable.

An example of this method is the estimation of the quantity of sugar in a solution from the rotation. Measurements of pure sugar solutions have shown that the rotation is by no means exactly proportional to the concentration. Correction must be made for this in very accurate work. The presence of other substances, as salts, alcohol, etc., affect the rotation, but only to a slight extent.

Similar to this is the estimation of concentration by means of the colour, if only one substance is present which has a marked light-absorption. The validity of Behr's law, that the extinctioncoefficient is proportional to the content of the coloured material, is taken for granted; there are, however, deviations in certain cases, so that the law must be tested in each new application of it.

A colorimeter is employed in making these measurements. It consists of two tubes closed below by plane glass plates; in the one is placed the liquid under investigation, to a known height in the tube. In the other the height of a standard liquid is varied until both tubes appear of the same colour when viewed vertically. Many devices have been employed to make this comparison convenient and accurate; in one of the simplest and best, two parallel mirrors are placed above the tubes at an inclination of 45° to their axes. Part of the silvering is removed from the front one; when the other is viewed through the opening, the light is seen surrounded by the light from the first one; this permits of very accurate adjustment of the colour of the two columns of liquid. The error introduced by the slight asymmetry of this arrangement can be ascertained by preliminary experiments, and allowed for (Donnan, 1896). Theoretically better is the use of the Lummer-Brodhun cube.

Group Properties.—Between the general properties which occur in all substances, and special properties which are individual, there are intermediate properties which are common to large or small groups of substances. In the first place, there are the colligative properties of gases and dilute solutions, from the measurement of which important conclusions may often be drawn. An example of this is the estimation of the degree of dissociation of certain compounds from the gas density. The value, about 140, found for phosphorus pentachloride, proves that a compound PCl_5 is certainly not present in the vapour; but it does not indicate what substances are actually there. But if it is otherwise known what is present, the relative amounts can be ascertained from the observed vapour-density, as was shown in the case of nitrogen peroxide (p. 306).

A very wide field was opened up by the extension of the gas laws to dilute solutions. It has already been mentioned how it has led to one of the most important advances of modern chemistry, the theory of free ions.

Ions.—The idea of free ions brought with it a new series of problems regarding their nature and amounts. As to the former, the question of their composition in special cases, such as in the formation of complex compounds, can be answered by applying the criterion of double decomposition: groups which can take the place of known ions in salts are to be regarded as ions. A further guarantee for the results is afforded by the phenomena of migration: constituents which wander to the anode (p. 389) belong to the anions, and conversely.

Electrolytic conductivity is a certain proof of the presence of ions. If there is any uncertainty as to whether the conduction is metallic or electrolytic, the appearance of polarisation after the passage of a current will give the information. A still more certain proof is the existence of a potential when the substance is connected up with two different metals to form a cell. If the conductor is metallic, the electrometer will show no potential. The metals selected should be far apart in the potential series, *e.g.* zinc and platinum; to eliminate accidental compensations, the experiment should be repeated with other pairs of metals.

An approximate estimate of the concentration of the ions may be made from the observed electric conductivity. The migration velocity of the different ions (with the exception of hydrion and hydroxidion, whose presence is easily recognised by the acid or alkaline reaction) is much the same, so that an approximate idea may be obtained by means of the figures and rules given on p. 390 and p. 392.

After all, conductivity is only a group reagent for ions in general, showing their existence, but not their nature. But if this is known, the conductivity is an excellent means of estimating the concentration of ions; this application has been explained in a particular case on p. 404.

In many cases there are so many kinds of ions present that the conductivity affords no information as to the amounts of each kind. Specific reactions of single ions come in here. These occur in the chemical equilibria with solid phases (p. 426); from the diminution of solubility of a sparingly soluble substance the concentration of one of its ions can be found.

Another means which can be employed in cases with very small concentrations of an ion consists in the measurement of the potential between the solution and an electrode which is in equilibrium with the ion. An example of this has already been given (p. 447).

Velocity of Reaction.—One of the characteristics of chemical equilibrium is that any possible displacement of the system requires or yields an infinitely small amount of work. Its determination is thus a problem of energetics, and it is definitely fixed if the interdependence of the work and the relative amounts of the substances are known.

That a chemical reaction, with an appreciable velocity, will take place if the general condition of equilibrium is not fulfilled, can be demonstrated from the principles of energy; it can also be shown that, under otherwise equal conditions, the velocity with which the reaction will proceed to equilibrium will be proportional to the distance from equilibrium. How this distance can be measured follows from the form of the laws of the velocity of reaction (p. 289 *et seq.*).

These show that a reaction will take place with finite velocity, and, secondly, that the successive parts of the reaction are completed in times which stand in regular relation to each other; but they do not show what time is required for a given fraction of the reaction to take place. The laws are satisfied, whether the transformation of one per cent of the total requires a second or a year.

No estimate of the absolute velocity can be made from the relation of the velocities of two opposed reactions, which lead to an equilibrium. If one velocity and the equilibrium are given, the other velocity is also defined; but from the equilibrium alone the ratio of the velocities can be deduced, and their absolute values can be any amount.

These considerations are strikingly confirmed by experience. Circumstances which have little or no effect on the equilibrium alter the velocity to an extraordinary extent. A well-known example of this is the formation of esters from acids and alcohols; while the velocity is increased a thousand-fold by a temperature increase of about 100°, the equilibrium is, owing to the small heat of reaction, displaced to a hardly recognisable extent. Further, the effect of raising the temperature is fundamentally to increase the velocity, while equilibrium may be displaced in either direction.[1] The general rules have been already given (p. 297).

Other conditions beside temperature have a great effect on the velocity, above all others the presence of other substances. As stated on p. 298, such an effect always exists; but it is in many cases not large, and has not attracted much attention. But in other cases very small quantities of foreign substances bring about enormous changes in the velocity. The change may be positive or negative, *i.e.* either increase or decrease of velocity.

These substances are called catalysers, positive or negative according as they accelerate or retard the reaction. For their action see p. 298 *et seq.*

Kinetic Analysis.—Owing to these various strong influences, there is no simple connexion between the velocity of reaction and the general stoichiometric properties of substances. It is, however, a very wide and delicate means for the more exact analysis of chemical processes.

The ordinary methods of preparation take into account only the beginning and the end, and the assumption is commonly made that there is only one step between them. It has been already established in many cases that an apparently simple process passes through a large number of intermediate stages, some of which can be proved under suitable conditions. There is apparently no more simple reaction that the oxidation of the base metals by free oxygen. And yet it is known that the metal and oxygen do not directly combine, since in pure oxygen even the very positive metals are not measurably

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[1] There are a few cases in which the velocity falls off with rise of temperature. It is not yet known what special circumstances are responsible for this.

oxidised. Water is almost always necessary, and hydrogen peroxide is regularly found to be one of the products.

The law of intermediate stages is to be regarded as the general ground of this complication: according to it, the most stable product of a reaction does not result, but the most unstable which can result from the point of view of energy. There are doubtless other constitutive influences at work, which decide which of the possible reactions does take place. As to this, however, no general laws are known.

In the investigation of reaction velocities we have a means of obtaining information on such questions. According to the laws of chemical kinetics the velocity of a process is proportional to the concentration of all the substances participating in it. If the general chemical equation, $aA + bB + cC + \dots = xX$, represents the process, which we shall assume, for the sake of simplicity, to be complete, the reaction velocity is proportional to the product $(A)^a . (B)^b . (C)^c \dots$, where the letters in brackets denote the concentrations of the given substances, and the small letters their molar coefficients. If now a reaction is made up of several stages, the velocity of each step is expressed by a formula for this single reaction, and the formula for the total process is of no account in the equation for the velocity.

The question is undoubtedly more complicated on this account. Fortunately, cases are frequent in which most of the reactions are very rapid, and only one of them slow. This one defines the whole reaction from the point of view of time, and the equation for the whole velocity of reaction depends on its chemical equation. We may assume that the slow reaction corresponds to the first stage of the total process, for if the first stage is a rapid process, its product will be found as the reaction product, which can be obtained if the possibility of further transformation is removed.

The method of isolation of the reaction factors (Ostwald, 1896) is applied in the kinetic analysis of the process in such a case. The reaction is so carried out that all the concentrations except one are relatively very large; their influence on the reaction is thus excluded (since they change to a very slight extent during the reaction), and the influence of the substance present in small quantity alone remains. For instance, in the above reaction A is taken in small amount, B and C in large amount. The two last concentrations become constant, and the velocity of reaction is proportional to $(A)^a$, whence the order of the reaction for the substance A is determined. Similarly with B and C, and thus the left side of the true equation for the velocity is obtained with the correct molar coefficients. Although this does not decisively settle the right side of the equation, yet it generally places us on secure ground from which the further question may be more easily answered.

An illustration of the value of this method may be given: the catalytic influence of molybdic acid on the oxidation of iodide ion by means of hydrogen peroxide. The order of reaction for the hydrogen peroxide alters on addition of molybdic acid, from which the important result for the theory of catalysis is obtained, that at least in this case there is an intermediate reaction between them (Bredig and Brode, 1901).

CHAPTER XXVIII

STOICHIOMETRIC RELATIONS

General.—A law whose validity has always been assumed is that the affinity of substances stands in regular and unmistakable relation to their composition and constitution. And yet a quite important part of the usual chemical systematics is based on great differences in the affinity, the perception of which did not necessitate quantitative measurements: later quantitative research supplied the detail and exact numerical data to fill in this general ground plan.

The second stage of development has not yet made much advance, and, in particular, the available material still awaits systematic working up and arrangement. No attempt is made in the following pages to work out such a system, and this final chapter of the book is rather in the nature of an indication of what could and should be done in this direction, than the embodiment of completed researches.

As chemical reactions of ions can be more easily and quickly observed than those of other substances, it is natural that in the order of historical development affinity problems should be at first confined to these phenomena. The affinity tables of last century contained only salt reactions, and when, at the end of it, the quantitative treatment of affinity began to develop, it was again the problem of salt formation which was first attacked.

It was not until the second half of the century that non-electrolytes claimed scientific attention. As the attempt to transfer ideas gained from the study of electrolytes, as embodied in the electrochemical system of Berzelius, to this new class of compounds was bound to fail, the mistake was made of rejecting these views as erroneous; and because binary formulæ would not fit alcohols and hydrocarbons as well as salts, salts were made to fit unitary formulae like the hydrocarbons. It is only in our own times that this has been recognised to be as great a mistake as it was to apply electrochemical dualism to organic compounds.

For the considerations of this chapter the chemistry of ions must be separated from that of non-ions; the two have widely different characteristics. The difference to some extent coincides with the traditional difference between inorganic and organic chemistry, but only partially, and it would be a serious mistake to represent inorganic chemistry as the chemistry of ions. For not only are there numerous reactions of inorganic chemistry which cannot be represented from the ionic point of view, but organic chemistry contains innumerable substances in the ionic form. Several very important stoichiometric properties of ions were discovered and worked out on organic material.

History.—The history of this problem commences with the affinity tables, *i.e.* with the order in which substances are displaced from analogous compounds. Stahl gave the problem this form; it was then taken up by Geoffroy and brought to a conclusion by T. Bergmann in the last quarter of the eighteenth century. These tables were at first supposed to express only the qualitative order of the affinity, but later also the quantitative order. That they were given up as rapidly as they had been adopted, was owing to the inadequate nature of the assumptions on which they were based.

The supposition was that affinity was to be regarded as a kind of mechanical force. Just as a larger force overcomes a smaller, with the result that the body moves in the direction of the greater, so chemical reactions take place exclusively in the direction of the greater affinity. This basis was attacked by Berthollet at the beginning of last century, and although he did not succeed in putting his new views as to the occurrence of chemical equilibrium into developable form, the affinity tables vanished after their appearance.

On the discovery of the laws of stoichiometry at the beginning of last century, followed soon after by the development of organic chemistry, the question of the laws of chemical affinity receded into the background. The reactions of carbon compounds were apparently so little the result of greater or smaller forces of affinity, and so much dependent on the "arrangement of the atoms," that Dumas in his first attempts to develop the theory of types would admit only the latter as having any influence on reactions. Although the error of such a view was soon recognised, the circumstance remains that affinity problems in the strict sense scarcely arose in organic chemistry. Even when Berthelot and Péan de St. Gilles discovered and studied in the formation of esters from acids and alcohols (1862) an example belonging to organic chemistry, in which the partial and conditional course of the reaction with time could be very plainly followed, many years elapsed before the revival of the development of Berthollet's theory by Guldberg and Waage (1867) rendered possible the foundation of a systematic doctrine of affinity.

The first to advance in the new direction was J. Thomsen (1868), whose thermochemical investigations had for their aim the affinity relations between acids and bases. The most essential feature of this research, after the proof of the validity of the law of mass-action, was the discovery that the affinity of acids, as derived from their equilibria, was quite independent of their heats of neutralisation. This finally set aside the error that the two are proportional.

After Thomsen's investigations came those of Ostwald (1877 onwards) which showed that the most widely different reactions of acids are proportional to one another, and that, therefore, specific affinity coefficients can be assigned to them (as also to bases, as was shown somewhat later) which change with the temperature and the concentration, but are independent of the nature of the reaction.

According to Arrhenius's theory of free ions these specific coefficients are defined by the concentration of free hydrogen ions or hydroxyl ions present, and the equilibrium phenomena of electrolytes were traced to the dissociation coefficients of the substances concerned (p. 405).

Thus the affinity problem for homogeneous equilibrium in electrolytes is really solved, if the coefficients are known. The investigations have been principally made on aqueous solutions; other solvents present certain difficulties, which have, however, been for the most part overcome.

The Affinity Constants of Acids.—As was shown on p. 405, the dissociation constant k is given by the formula

$$\frac{a^2}{(1-a)v} = k,$$

in which a is the fraction of substance dissociated and v is the dilution. The formula contains a single constant k, determined by the nature of the substance, and this constant is the required measure of the chemical affinity under the given conditions.

To grasp its significance let us imagine half of the substance to be dissociated. Putting $a = \cdot 5$ we get

$$\frac{1}{2} = kv\,;\ 2\,k = \frac{1}{v}\,.$$

2 k is thus equal to the reciprocal of the dilution, *i.e.* to the concentration, for which the electrolyte is exactly half dissociated.

The measurement of electric conductivity is the simplest and most exact method of measuring k. We have seen (p. 392) that the extent of dissociation a is the ratio between the corresponding molar conductivity μ and the limiting value of the conductivity for infinite dilution, $\mu\infty$.

The stoichiometric relations of the constant k are particularly noticeable in the organic acids (Ostwald, 1889), and will be reproduced for a few typical cases. As the constant derived from the formula $\frac{a^2}{(1-a)v}=k$ is inconveniently small, the larger number $K=100\ k$ will be used in what follows. All the numbers were determined from the electric conductivities at 25°.

The constants for the fatty acids were found to be

Acid.		K.
Formic	$H . CO_2H$	·0214
Acetic	$CH_3 . CO_2H$	·00180
Propionic	$C_2H_5 . CO_2H$	·00145
Butyric	$C_3H_7 . CO_2H$	·00115
Isobutyric	$C_3H_7 . CO_2H$	·00159
Isovaleric	$C_4H_9 . CO_2H$	·00161
Caproic	$C_5H_{11} . CO_2H$	·00147

The values of the three first members decrease continuously; the substitution of CH_3 for hydrogen thus lowers the activity of the acids. After the third member the values vary irregularly by small amounts. The substitution, therefore, when taking place at a distance from the carboxyl group exerts no noticeable influence on the latter: other influences then come into play, but these are at present beyond our knowledge.

It is somewhat remarkable that the isomeric butyric acid and isobutyric acid should have almost equal values. This is not of frequent occurrence, isomeric compounds having mostly very diverse values.

If we introduce chlorine into acetic acid in place of hydrogen, the constant is considerably raised.

Acid.	K.
Acetic	·00180
Monochloracetic	·155
Dichloracetic	5·14
Trichloracetic	30 (?)

Inquiring into the manner in which changes in the complex affect the carboxyl and thus the constant, we may first of all ask whether the latter is altered by the same amount or in the same ratio by the changes. A glance at the numbers is sufficient to show that the latter alternative only is possible. The differences for the substitution of one atom of hydrogen by chlorine are ·153, 4·99, and 25, while the corresponding ratios are 86, 33·2, and 6. That the last numbers are not equal is not surprising (p. 226), for the changes are not equal, chlorine in the first case entering a molecule in which no chlorine is already present, while in the second case the substitution is effected in the group CH_2Cl, and in the third case in the group $CHCl_2$. The three changes are thus not the same but only similar, and the corresponding ratios are consequently not equal but only of the same order.

The influence of the substituent chlorine on the acid properties of acetic acid is very considerable; we must therefore attribute to it important "acidifying" properties. The way in which this action is exerted can at present be scarcely indicated even hypothetically. Berzelius assumed that the atoms of chlorine were charged with a somewhat large excess of negative electricity and therefore exerted a strong attraction on positively charged bodies, like the metals. This hypothesis is difficult to reconcile with the knowledge we now possess of the behaviour of electricity, since the substances show no free electricity. We still retain from the old theory the designation of the elements as positive or negative according as they incline to form basic or acid compounds.

If instead of chlorine we take some other "negative" substituting radical, we in the same way obtain an increase in the strength of the acid. Thus, for example, we have

Acid.		K.
Acetic	$CH_3 . CO_2H$	·00180
Monobromacetic	$CH_2Br . CO_2H$	·142
Cyanacetic	$CH_2(CN)CO_2H$	·370
Thiocyanacetic	$CH_2(SCN)CO_2H$	·265
Carbamylthioglycollic	$CH_2(S . CO . NH_2)CO_2H$	·0246
Thioglycollic	$CH_2(SH)CO_2H$	·0225
Glycollic	$CH_2(OH)CO_2H$	·0152

The constant for bromacetic acid ·142 is not very different from that for chloracetic acid ·155, as we might expect from the agreement between hydrobromic and hydrochloric acids. On the other hand, the constant of cyanacetic acid is considerably greater: cyanogen is thus a much more "negative" substituent than chlorine or bromine. Nevertheless hydrogen cyanide is so weak that it scarcely deserves the name of acid. This circumstance forces us to the conclusion that hydrogen cyanide is not at all comparable with the halogen hydracids.

The radical thiocyanogen is likewise of much greater influence than chlorine; but the constant does not reach the value for cyanacetic acid. Thiocyanic acid is a genuine hydracid, and quite comparable with hydrochloric acid in point of strength.

The extraordinary enfeeblement suffered by this acid on taking up the elements of water to form carbamylthioglycollic acid, a substituted acetic acid in which the residue of thiocarbamic acid replaces a hydrogen atom, is very remarkable. The constant sinks to a tenth of its former value. The cause is probably to be sought in the action of the basic group NH_2, which is introduced.

The replacement of the hydrogen of acetic acid by hydroxyl also produces a considerable rise in the strength of the acid, the constant of glycollic acid being some eight times greater than the constant of acetic acid. Hydrosulphyl, SH, in the same position occasions a somewhat greater increase than hydroxyl, as we might expect from hydrogen sulphide being a stronger acid than water.

If a second hydroxyl is introduced into acetic acid, glyoxylic acid is produced:

Glyoxylic acid $CH(OH)_2CO_2H$ ·0474

The ratio between acetic acid and glycollic acid is 1 : 8; between the latter and glyoxylic acid 1 : 3. The second substitution of hydroxyl is thus less effective than the first. This result may be compared with the corresponding one for substitution of chlorine.

With thioglycollic acid we may compare thioacetic acid. We have:

Thioacetic acid $CH_3.COSH$ ·0469

while the constant for thioglycollic acid is ·0225, not so much as half. The reason lies in the much closer connexion in thioacetic acid between the entrant "negative" sulphur atom and the acid hydrogen atom, the action of the sulphur coming much more strongly into play.

The hydroxypropionic acids are quite parallel to the corresponding derivatives of acetic acid. We have two monohydroxy-acids however, and these have different constants.

Acids.		K.
Propionic	$CH_3.CH_2.CO_2H$	·00145
Lactic	$CH_3.CH(OH)CO_2H$	·0138
β-Oxypropionic . . .	$CH_2(OH).CH_2.CO_2H$	·00311

While the hydroxyl in the α-position increases the constant of propionic acid tenfold, the same radical in the β-position only acts with the factor 2·3. This is a very clear case of the general principle that the action of the various elements on the affinity depends not only on their nature, but also on their "position" or constitution.

If a β-hydroxyl is introduced into lactic acid, glyceric acid is the product.

Glyceric acid $CH_2(OH).CH(OH)CO_2H$ ·0228

The ratio of the constant to lactic acid is 1·7, while the ratio between propionic acid and β-oxypropionic acid is 2·3. The alteration is in both cases of the same order, but smaller where the substituting radical is already present. This is exactly what we found for the chlorine and hydroxyl substitution products of acetic acid.

A similar influence of the position of the substituent is seen in the case of levulinic acid.

Levulinic acid $CH_3.CO.CH_2.CH_2.CO_2H$ ·00255.

Apart from the position of the carbonyl group this acid is related to valeric acid as glyoxylic acid is to acetic acid. The ratio of the former acids is, however, only 1·5 : 1, while the ratio between the latter is 26 : 1. The enormous difference can only be ascribed to the distance of the oxygen atom (or the equivalent two hydroxyls) from the carboxyl in levulinic acid.

Further examples of the influence of position are to be found in the following substances:

Acids.		K.
α-chloropropionic .	$CH_3 . CHCl . CO_2H$	·15
β-chloropropionic .	$CH_2Cl . CH_2 . CO_2H$	·0086
β-iodopropionic . .	$CH_2I . CH_2 . CO_2H$	·0090
trichlorolactic . .	$CCl_3 . CHOH . CO_2H$	·465
α-chlorobutyric . .	$C_2H_5 . CHCl . CO_2H$	·14
β-chlorobutyric . .	$CH_3 . CHCl . CH_2 . CO_2H$	·0089
γ-chlorobutyric . .	$CH_2Cl . CH_2 . CH_2 . CO_2H$	·0026
trichlorobutyric. .	$CH_3 . CHCl . CCl_2 . CO_2H$	10
nitrocaproic . .	$CH_3 . CH(NO_2) . C(CH_3)_2 . CO_2H$	·0123
dinitrocaproic . .	$CH_3 . C(NO_2)_2 . C(CH_3)_2 . CO_2H$	·0694

The influence of position is more marked the stronger the effect of the substituent itself is.

In the case of trichlorolactic acid the difference is very marked. The constant of lactic acid is ·0138, and the three chlorine atoms have increased this in the ratio of 34 to 1. The same substitution for acetic acid gives an increase from ·0018 to 30, a ratio of 1 : 16000, *i.e.* the influence in the latter case is some 400 times greater.

Mononitrocaproic acid with the constant ·0123 conducts 8·5 times better than caproic acid. It cannot therefore be an α-compound; for the nitro group proves itself to be far more negative than chlorine, and chlorine in the α-position effects an eighty-fold multiplication of the constant. The number, however, corresponds very well with the supposition that the nitro group is in the β-position, an assumption already made from the chemical behaviour of the substance. The introduction of a second nitro group occasions an increase of the constant of mononitrocaproic acid in the proportion of 5·6 to 1. The factor for the second group is smaller than for the first, a fact in agreement with what we have already found.

The influence of position can be investigated much more extensively for the derivatives of benzoic acid than is the case with acids of the fatty series. For example, the following constants have been observed:

Acid.		K.
Benzoic	$C_6H_5CO_2H$	·0060
o-Oxybenzoic	$C_6H_4(OH)CO_2H$	·102
m-Oxybenzoic		·0087
p-Oxybenzoic		·00286

Benzoic acid itself is more powerful than the higher fatty acids, stronger even than acetic acid. Phenyl is in general more negative than methyl, for phenyl alcohol or phenol has the character of a weak acid, which is not the case with methyl alcohol. The introduction of hydroxyl is extremely different in its effect according as it occupies the ortho, meta, or para position. In the o-position its influence is greatest—the constant is multiplied by 17. The increase is only in the ratio 1·4 : 1 when it occupies the m-position, while in the p-position its entrance effects a weakening of the acid, the constant sinking to about half its former value.

From the effects produced by the introduction of hydroxyl into the three different positions in benzoic acid, we can estimate very closely the constants of all the other hydroxybenzoic acids. The following numbers have been obtained for these substances, the position of the hydroxyls with reference to the carboxyl group being indicated by the numbers affixed to the formula, counting from the carboxyl group as 1.

Acid.		K.
Oxysalicylic	$C_6H_3(OH)_2CO_2H$ (2,3)	·114
Oxysalicylic	$C_6H_3(OH)_2CO_2H$ (2,5)	·108
α-Resorcylic	$C_6H_3(OH)_2CO_2H$ (2,6)	5·0
β-Resorcylic	$C_6H_3(OH)_2CO_2H$ (2,4)	·052
Protocatechuic	$C_6H_3(OH)_2CO_2H$ (3,4)	·0033
s-Dioxybenzoic	$C_6H_3(OH)_2CO_2H$ (3,5)	·0091
Gallic	$C_6H_2(OH)_3CO_2H$ (3,4,5)	·0040
Pyrogallol-carboxylic	$C_6H_2(OH)_3CO_2H$ (2,3,4)	·055
Phloroglucin-carboxylic	$C_6H_2(OH)_3CO_2H$ (2,4,6)	2·2

According to what we have already seen, the simultaneous action of several substituents was mostly of such a character that each contributed a factor to the constant according to its nature and position. The factor was to some extent, but not entirely, independent of what already existed within the molecule, being less for the second substitution of the same group than for the first.

Thus we should be led to expect that 2, 3-oxysalicylic acid would be somewhat stronger than salicylic acid; because the m-hydroxyl, which has entered, increases the constant slightly (see above). Salicylic acid has the constant ·102, oxysalicylic acid ·114, thus confirming our expectation.

In 2, 5-oxysalicylic acid the hydroxyl likewise occupies the m-position; the two isomeric acids have therefore both the hydroxyl groups equally distant from the carboxyl. Nevertheless they are somewhat different; the 2, 5-acid being indeed stronger than salicylic acid, but not so much so as the 2, 3-acid. This proves that the action of the separate substituents is to a small but still noticeable extent dependent on the others.

If the two formulæ are written down in the ordinary way with the benzene nucleus represented by a hexagon, it will be seen that the position 2, 3 is more favourable to the mutual action than the position 2, 5.

β-Resorcylic acid (2, 4) is produced from salicylic acid by the introduction of hydroxyl into the p-position; it should therefore be only half as powerful as the latter. Its constant ·052 is, in fact, only half that of salicylic acid, ·102.

In α-resorcylic acid there are two hydroxyls in the o-position. The first hydroxyl introduces the factor 17, the second hydroxyl supplies the factor 49. This is contrary to what we found before (p. 566), viz. that the second of two like substituents effected a smaller increase than the first. This new phenomenon, however, is not a singular instance, as may be seen from the following figures:

Acid.		K.
Gallic	$C_6H_2(OH)_3CO_2H$	·0040
Monobromogallic	$C_6HBr(OH)_3CO_2H$	·059
Dibromogallic	$C_6Br_2(OH)_3CO_2H$	1·21

Since the three hydroxyls occupy the places 3, 4, 5, the bromine atoms must both be in the o-position. The first bromine atom increases the constant 15 times, the second atom 20 times. Here also, then, the second substituent acts more powerfully than the first. From this it follows that the o-position in the benzene nucleus conditions quite different actions from the α-position in fatty chains. A comprehensible geometrical explanation of these peculiar relations is not far to seek, but we cannot enter upon it here.

Protocatechuic acid with one hydroxyl in the m-position and the other in the p-position, should, owing to the latter, be only half as strong as m-oxybenzoic acid. This also is actually found to be the case.

Symmetrical dioxybenzoic acid has two m-hydroxyls and consequently a constant ·0091, exceeding slightly that of m-oxybenzoic acid, ·0087. All the dihydroxybenzoic acids thus obey the law that the constants of affinity of multi-substituted acids appear approximately as products of the factors due to each of the substituents separately.

It is also possible to calculate with a considerable degree of accuracy the constants for all the known trioxybenzoic acids. Thus gallic acid is the p-oxyderivative of symmetrical dioxybenzoic acid; its constant should therefore be about half that of the latter. The actual numbers are ·0040 and ·0091. Pyrogallol-carboxylic acid is the p-oxyderivative of oxysalicylic acid; the constants are ·055 and ·114—again in the ratio of 1 : 2. Phloroglucin-carboxylic acid, lastly, is the p-oxyderivative of α-resorcylic acid, and their respective constants are, according to expectation, 2·2 and 5·0. These relations hold good with such certainty that the constants for the three unknown trioxybenzoic acids can be given beforehand, so that once the acids are prepared, a simple measurement of their electric conductivity will suffice to determine their constitution. Other substituents in benzoic acid behave quite similarly to hydroxyl.

Acid.		K.
o-Chlorobenzoic	$C_6H_4Cl . CO_2H$	·132
m-Chlorobenzoic		·0155
p-Chlorobenzoic		·0093
o-Bromobenzoic	$C_6H_4Br . CO_2H$	·145
m-Bromobenzoic		·0137
m-Fluorobenzoic	$C_6H_4F . CO_2H$	·0136
m-Cyanobenzoic	$C_6H_4(CN)CO_2H$	·0199
o-Nitrobenzoic	$C_6H_4(NO_2)CO_2H$	·66
m-Nitrobenzoic		·0345
p-Nitrobenzoic		·0396
o-Nitrosalicylic (1, 2, 3)	$C_6H_3(OH)(NO_2)CO_2H$	1·57
p-Nitrosalicylic (1, 2, 5)		·89
Bromonitrobenzoic (1, 2, 6)	$C_6H_3Br(NO_2)CO_2H$	1·4

These numbers again call for a few remarks. Chlorine as a substituent in benzoic acid acts quite differently from hydroxyl. Whereas o-chlorobenzoic acid is only a little stronger than salicylic acid, m-chlorobenzoic and p-chlorobenzoic acid are more powerful than the corresponding hydroxyl acids. Chlorine in all three positions increases the constant. Bromine behaves very similarly to chlorine, only, while the ortho compound is somewhat stronger, the meta compound is distinctly weaker, than with chlorine. m-Fluorobenzoic acid has exactly the same constant as the corresponding bromine compound—an unexpected result, as hydrofluoric acid is much weaker than hydrochloric acid. Cyanogen shows its strong negative character in this case also, its influence surpassing that of chlorine; as cyanacetic acid is considerably stronger than chloracetic acid, so m-cyanobenzoic acid is superior in point of strength to the corresponding chlorine compound.

A group still more negative than cyanogen is the radical NO_2. In the ortho compound the constant of benzoic acid is increased one hundredfold, the constant of the meta acid is 5·7 times, and of the para acid 6·6 times greater than that of the unsubstituted compound. Here the p-nitrobenzoic acid appears stronger than m-nitrobenzoic acid, the opposite being usually the case. This circumstance renders it probable that the complex of six carbon atoms composing the benzene nucleus is not a rigid aggregate.

The two nitrosalicylic acids contain the nitro group in the meta position with respect to the carboxyl. They are both considerably stronger than the parent substance, and the factor in both cases is greater than that connecting benzoic and m-nitrobenzoic acid. Similar phenomena have already been noticed (p. 570).

Bromonitrobenzoic acid, finally, contains the nitro group in the ortho, and bromine in the meta position. This latter, if we take the numbers for benzoic and m-bromobenzoic acid as basis, would more than double the constant. Thus, since o-nitrobenzoic acid has a constant of ·66, we should expect for bromonitrobenzoic acid the number 1·4; and this is the result of actual measurement.

Up till now we have considered almost exclusively compounds containing negative substituents, *i.e.* such as heighten the acid character of a substance. We met with the group methyl, however, which (p. 566), under certain circumstances (*e.g.* in the passage from formic to acetic acid), diminished the value of the constant. But this is not always the case. When methyl is substituted for hydroxyl hydrogen in glycollic acid the constant becomes greater. Ethyl acts less powerfully than methyl.

Acid.		K.
Glycollic	$CH_2OH . CO_2H$	·0152
Methylglycollic . .	$CH_2O(CH_3) . CO_2H$	·0335
Ethylglycollic . .	$CH_2O(C_2H_5) . CO_2H$	·0234

Phenyl has already been recognised as having a greater acid-forming capacity than methyl, so we cannot be surprised that phenylglycollic, K = ·076, acid is much stronger than glycollic acid itself.

The amido group, NH_2, distinctly weakens the acid properties of substances into which it enters. For instance, its introduction into benzoic acid gives the following numbers:

Acid.		K.	
Benzoic	$C_6H_5 . CO_2H$	·0060	
o-Amidobenzoic	$C_6H_4(NH_2)CO_2H$	·0009	(approx.)
p-Amidobenzoic		·0010	
m-Amidobenzoic		·0012	

The constants of the amido acids cannot be determined with precision owing to experimental difficulties. They are considerably less than the constant of benzoic acid.

If an acetyl group is introduced into the amido group, the basic properties of the latter are not only balanced, but outbalanced; the constants of the ortho and meta acetamidobenzoic acids are greater than that of benzoic acid. In the para compound the weakly negative radical effects a diminution, exactly as we found to be the case with hydroxyl (p. 570).

Acid.		K.
Benzoic	$C_6H_5 . COOH$	·0060
o-Acetamidobenzoic	$C_6H_4(NH . CO . CH_3)COOH$	·0236
m-Acetamidobenzoic		·0085
p-Acetamidobenzoic		·0052

The foregoing examples will suffice to show the character of the information derived from measurement of the constant of electrolytic dissociation, K; a complete enumeration of the results already obtained in this direction would be out of place here. Wegscheider (1902) has compiled a table of factors, with which the constant of the original acid is to be multiplied when a substituent enters any given position. It is given below.

	Position in saturated chain of aliphatic series.							
Radical.	α	β	γ	δ	ε	ζ	η	θ
Cl	90	6·2	2·0	1·27	...	...	...	...
Br	76	7·3	1·76	1·19	...	...	...	...
I	42	6·7	1·53	1·06	...	...	...	...
F	...	...	...	...	...	...	...	...
CN	205	...	...	...	...	...	...	...
NO_2	...	12·5	...	...	...	...	...	...
OH	8·4	2·31	...	...	...	...	...	...
OCH_3	18·6	...	...	...	...	...	...	...
OC_2H_5	13	...	...	...	...	...	...	...
SH	12·5	...	...	...	...	...	...	...
CH_3	·74, 1·10, ·62	1·12	1·00	·90	·90	1·10 ?	·78 ?	...
C_2H_5	·83, 1·31, ·66	1·20	·98	·81	·99	·85	...	...
C_6H_5	3·1	1·7	...	...	...	...	...	...
SO_3CH_3	...	...	...	...	...	...	...	...
COOH	34	2·4	1·67	1·2	1·2	1·2	...	1·2
$COO . CH_3$	...	2·4	...	...	...	...	...	...
$COO . C_2H_5$	27	2·25	...	...	...	...	...	1·28 ?

	Position in aromatic nucleus.		
Radical.	o	m	p
Cl	22	2·58	1·55
Br	24	2·28	...
I	...	2·72 ?	...
F	...	2·3	...
CN	...	3·3	...
NO_2	103	5·75	6·60
OH	17	1·45	·48
OCH_3	1·36	1·08	·53
OC_2H_5	...	...	...
SH	...	...	...
CH_3	2·0	·86	·85
C_2H_5	...	...	...
C_6H_5	...	...	...
SO_3CH_3	...	11	...
COOH	10·2	2·39	2·62
$COO . CH_3$	11	...	2·8
$COO . C_2H_5$	9·2	...	...

Affinity of the Elements.—On turning from this special province to more general questions, we leave behind the basis of quantitative knowledge. We may go back to the elements, and attempt to investigate the relations between them and their ions. This leads to the question of the tendency to form ions, or, in figurative language, the affinity of the elementary substances for electricity. Although no figures are available, the differences are so great that systematic connexions are easily recognised.

There is a marked falling off in the power of forming ions in the natural families in the periodic arrangement of the elements. Along with this the valency of the ion depends on the series to which it belongs. Series I., on p. 154, consists of the alkali metals, all with univalent kations, which are much more stable than the neutral elements; their most important reactions consist in their transformation into the ionic state, or into the allied state of solid salt. The elements of the sub-series, Cu, Ag, Au, show their slight affinity with the series by their much smaller ionic tendency, which rapidly falls off with increasing combining-weight. With this is united the power of forming complex ions which accompanies a smaller tendency to form elementary ions.

Series II. contains the elements which form bivalent kations. Here, too, the tendency is much greater in the main series of alkaline earths than in the sub-series of heavy metals. The last member, mercury, has to a marked degree the power of forming complex anions, which is only suggested in the lower members.

A similar state of affairs is found in Series III., but in it the ionic tendency is much smaller. It increases with the atomic weight in the main series, but falls off in the sub-series. The highest members again form ions with different valency.

The peculiarity that elements with the smallest combining-weight have the smallest tendency to form elementary ions is very pronounced in Series IV., for the lower members cannot form ions at all, and only the highest one, thorium, forms stable salts. In this series the difference between main- and sub-series is lost, the formation of ions being favoured by increase of formula-weight.

These elements possess very fully the power already indicated in the earlier members of the previous series, of uniting with oxygen to form compound anions. Simultaneously, variation in the valency of the ions is fully developed.

In the elements of Series V. are seen the first traces of elementary anions, in the formation of salt-like compounds in which these elements represent the acid. These compounds are either insoluble in water, or are decomposed by it; the ions do not exist in aqueous solution, but they may be present in the state of fusion. The anions containing oxygen are very important, while the elementary kations are confined to the highest members; they have the same valency. The first appearance of a compound kation containing oxygen, VdO, vanadyl, may be noticed.

Elementary bivalent anions are undoubtedly present in Series VI. The formation of anions containing oxygen is typically developed:

both elementary and compound oxygen-containing kations occur in the highest members.

The VIIth Series contains the typical elementary anions, the halogens. With the exception of the first they form anions containing oxygen; undoubted signs are present that the highest member, iodine, can form with oxygen compound kations.

The elements of the special group of the iron and platinum metals are distinguished by their ability to form ions with very different valency, and by their very marked tendency to form complex ions.

These indications of an ionic system might be very considerably extended. Abegg and Bodländer (1899) have shown in particular that the solubility of salt-like compounds and the formation of complexes are closely, and to some extent quantitatively, connected with the property of "electro affinity."

Organic Compounds.—When we turn from ions to the non-electrolytes of organic chemistry, we find, as has been already remarked, that a great part of systematic organic chemistry is based upon estimations of affinity properties. Constitutive differences, such as characterising oxygen as hydroxyl-, ketone-, aldehyde-, ether-oxygen, have been made on the ground of observations in decompositions and equilibria. Noteworthy beginnings of quantitative treatment have been made. Numerous and extensive researches of Menschutkin (from 1879) on the formation of esters from organic acids and alcohols have shown certain regularities at least for the limited region of homologous and analogous compounds. Thus normal primary alcohols (except methyl alcohol) are esterified at the same rate; the other primary alcohols and the unsaturated alcohols more slowly, and the secondary alcohols still more slowly; there are also differences among the various secondary alcohols. If the same alcohol is acted upon by different acids, the primary fatty acids show a decreasing velocity of esterification with rising molar weight. The secondary acids are much slower, and the tertiary acids slowest of all.

In recent times many researches with a similar object (Wegscheider, H. Goldschmidt and others) have yielded remarkable results, details of which can hardly be given here.

So, too, the mere hint must suffice that non-aqueous solutions give on the whole results similar to those already obtained in aqueous solution, except that they are not so simple.

For in a text-book devoted to general chemistry it would be out of place to give a detailed account of these relations, since they unquestionably belong to special inorganic and organic chemistry. The development of science in this direction has been so recent that they are only now beginning to find their way into the text-books. But it is universally felt that affinity problems will play a very important part in chemical systematics; and with this growth of the importance which will attach to relationships based on the principles of general chemistry, the cultivation of the science will also increase, and it will bear new fruit.

Still, however gratifying the extension of general truth has been in this direction, the diversity of actual phenomena cannot ever be completely represented; and every attempt to find the expression of this general truth in any given case leaves behind it an endless variety of other problems.

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